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COMPARISON OF DIFFERENT PACKAGING MATERIALS TO DETERMINE THEIR EFFECT ON AVAILABILITY AND EFFECTIVENESS OF 1-METHYLCYCLOPROPENE

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# COMPARISON OF DIFFERENT PACKAGING MATERIALS TO DETERMINE THEIR EFFECT ON AVAILABILITY AND EFFECTIVENESS OF 1-METHYLCYCLOPROPENE

By

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ABSTRACT

**COMPARISON OF DIFFERENT PACKAGING MATERIALS TO DETERMINE THEIR EFFECTS ON AVAILABILITY AND EFFECTIVENESS OF 1-MCP**

By

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The effects of corrugated board, high density polyethylene (HDPE), and wood (*Gmelina arboreus*) materials on available concentration of the ethylene action inhibitor 1-methylcyclopropene (1-MCP) was tested in sealed chambers at different relative humidities. In addition, the ability of 1-MCP to suppress ripening of banana in the presence of those materials was evaluated.

The concentration of 1-MCP declined in the chamber headspace in the presence of the materials tested, but the rate at which 1-MCP gas was removed differed markedly. The average percentage loss for HDPE and wood was between 10-12% at the conditions tested, while for corrugated fiberboard it ranged from 12% to 94%.

The loss of 1-MCP in the presence of corrugated board occurred more readily at higher RH, while increasing the amount of material in the chamber headspace and the initial concentration seem to play an important role in the rate at which 1-MCP was depleted from the treatment chamber.

In these tests, corrugated fiberboard altered the dose response of bananas because it affected the amount of 1-MCP present, thus markedly reducing the effectiveness of the compound.

To my wife, Paula and our wonderful kids, Maria Paula and Luis Eduardo,

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# INTRODUCTION

Postharvest losses in quantity and quality are a significant problem for most horticultural crops. The magnitude of postharvest losses in fresh fruits and vegetables is an estimated 5 to 25% in developed countries and 20 to 50% in developing countries, depending upon the commodity, cultivar and handling conditions. To reduce these losses, producers and handlers must understand the biological and environmental factors involved in deterioration, and use postharvest techniques that delay senescence and maintain the best possible quality (Kader et al., 2002).

Traditionally, temperature, humidity control and modified atmospheres have been used to maintain quality and delay over-ripening and senescence of fruits and vegetables.

During the last decade the use of compounds that specifically target and inhibit ethylene responsiveness have emerged as technologies which can be used to delay senescence and deterioration of perishable fruits, vegetables, potted plants, and cut flowers. Among these compounds, 1-methylcyclopropene is the most promising ethylene action inhibitor (Sisler and Serek, 1997).

Postharvest applications with 1-methylcyclopropene (1-MCP) are done on commodities already packaged and ready to be shipped for distribution and commercialization. Even though the impact of 1-MCP on the postharvest biology of several fruits, vegetables, and cut flowers has been studied, published data on

the equilibrium headspace concentrations of 1-MCP in the airspace of research and commercial treatment chambers is lacking.

The focus of this research is to investigate how the presence of packaging materials might affect the concentration of 1-MCP, with the consequent reduction in its potential effectiveness to delay ripening associated processes. To accomplish this, the research project was divided into two main topics: 1) determining how packaging material might compromise treatment dosages of 1-MCP for climacteric fruits (bananas were used as the model system), 2) evaluating the impact of (a) increased relative humidity in treatment chambers containing wood, high density polyethylene, and corrugated fiberboard on the initial concentration of 1-MCP over time, (b) increased amount of packaging material in the treatment chamber on the initial concentration of 1-MCP over time, and (c) increased levels of 1-MCP in the presence of various packaging materials on the effective dose available in the treatment chamber over time.

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CHAPTER 1

# LITERATURE REVIEW

## 1.1 Introduction

Plants produce hundreds of volatile compounds which can act as regulators and coordinators in the growth and development of tissues and whole plants. Ethylene ($C_2H_4$) is a volatile that has received considerably study as a regulator of plant growth. This unsaturated two-carbon gas has been shown to have biological and commercial importance (Abeles et al., 1992). Production of ethylene varies with the type of tissue, the plant species, and the stage of development. Fruits have two phases of comparatively high rates of ethylene production. The first is associated with cell division and rapid growth; the second phase is associated with ripening (Abeles et al., 1992).

The physiology and biochemistry of ethylene production in higher plants is described in the literature (McKeon et al., 1995; Salisbury and Ross, 1992; Abeles et al., 1992).

To synthesize ethylene in the plant, the amino acid methionine is converted to S-adenosylmethionine (SAM), which is the precursor of 1-aminocyclopropane-1-carboxilic acid (ACC), the immediate precursor of ethylene. ACC synthase, which converts SAM to ACC, is the main control site of ethylene biosynthesis. The conversion of ACC into ethylene is mediated by ACC oxidase. The synthesis and activities of ACC synthase and ACC oxidase are influenced by genetic factors and environmental conditions, including

temperature and concentrations of oxygen and carbon dioxide (Kader et al., 2002).

Horticultural commodities are classified according to their respiration and ethylene production rates. The terms climacteric and nonclimacteric are used to describe fruits that show a large increase in carbon dioxide and ethylene production rates coincident with ripening, and those that do not (table 1.1). Although the term climacteric was originally applied to increased fruit respiration, it subsequently included a rise in ethylene production (Abeles et al., 1992; Kader et al., 2002).

Ethylene is known to induce ripening-associated processes such as softening, color change, conversion of starch to sugars, loss of acidity, etc, in climacteric fruits (Davies, 1995; Mauseth, 1991; Raven, 1992; Salisbury and Ross, 1992).

Table 1.1 Fruits classified according to respiratory behavior and ethylene production rates.

| Climacteric fruits | | Nonclimacteric fruits | |
|---|---|---|---|
| Apple | Muskmelon | Blackberry | Lychee |
| Apricot | Nectarine | Cacao | Okra |
| Avocado | Papaya | Carambola | Olive |
| Banana | Passion fruit | Cashew apple | Orange |
| Biriba | Peach | Cherry | Pea |
| Blueberry | Pear | Cranberry | Pepper |
| Breadfruit | Persimmon | Cucumber | Pineapple |
| Cherimoya | Plantain | Date | Pomegranate |
| Durian | Plum | Eggplant | Prickly pear |
| Feijoa | Quince | Grape | Raspberry |
| Fig | Rambutan | Grapefruit | Strawberry |
| Guava | Sapodilla | Jujube | Summer squash |
| Jackfruit | Sapote | Lemon | Tamarillo |
| Kiwifruit | Soursop | Lime | Tangerine and |
| Mango | Sweetsop | Longan | madarin |
| Mangosteen | Tomato | Loquat | Watermelon |

Adapted from Kader et al., 2002.

The role of ethylene in ripening has been confirmed by showing that inhibitors of ethylene synthesis delay ripening. There are two classes of inhibitors of ethylene action: (a) mild toxicants that block ethylene action by slowing down cellular physiology (i.e. carbon dioxide, benzothiadiazole, ethylene oxide), and, (b) competitive inhibitors that combine with the ethylene receptor (a cell component that ethylene must bind to induce its physiological effects) preventing the cell from responding to ethylene (Abeles et al., 1992).

The biological activity of ethylene analogues follows binding rules similar to the binding of olefins to silver. This suggests that a metal is part of the ethylene binding site. Ethylene can be considered a soft base and can be expected to bind to metal ions, which are soft acids (Abeles et al., 1992).

In 1979, Sisler introduced the use of various volatile unsaturated ring compounds as inhibitors of ethylene action. Since that time, it has been found that many compounds interact with the ethylene receptor and modulate ethylene responses (Sisler et al., 1999).

Recently, it has become apparent that cyclopropene (CP) and 1-methylcyclopropene (1-MCP) are very effective blocking agents for the ethylene receptor, and can inhibit the ethylene response for extended periods. Exposure to as little as 0.5 nL $L^{-1}$ of these compounds for 24 hours protects carnations and bananas from the effects of ethylene for about 12 days at 25°C. An analog, 3,3-dimethylcyclopropene (3,3-DMCP), is also active, but requires about 1000 times the treatment concentration, and protects for only 7 days. In contrast, methylenecyclopropane, a compound whose double bond is outside the cyclopropene ring, is an ethylene antagonist, mimicking the effects of ethylene (Sisler et al., 1999).

These compounds act at a remarkably low concentration (Sisler et al., 2001). After 24 h of exposure to as little as 0.7 nL $L^{-1}$ cyclopropene or 1-methylcyclopropene, is sufficient to block ripening of bananas at 24°C for 12 days. A concentration of 500 nL $L^{-1}$ of 3,3-dimethylcyclopropene is required for 24 hours to block ripening for 7 days. It is not known why these large differences in response occur.

Among the cyclopropenes, 1-methylcyclopropene (hereafter abbreviated as 1-MCP) is the most promising ethylene action inhibitor (Sisler and Serek,

1997). Under normal environmental conditions it is a gas, stable at room temperature and has a non toxic mode of action (U.S. EPA, 2006).

## 1.2 Regulatory status of 1-MCP

On September 27, 1997, the United States Environmental Protection Agency (U.S EPA) received an application from Biotechnologies for Horticulture, Inc. to register EthylBloc® containing 0.43% of 1-methylcyclopropene as a plant growth regulator (U.S. EPA, 2006).

A notice of receipt of the application for registration of 1-methylcyclopropene as a new active ingredient was published in the Federal Register on March 10, 1999 (64 FR 11868) with a 30 day comment period. No comments were received as a result of this publication (U.S. EPA, 2006).

In April, 2000, the Agency received a petition from AgroFresh Inc., proposing the establishment of an exemption from the requirement of regulations for residues of the biochemical 1-MCP in or on all food commodities (U.S. EPA, 2006). A notice of filling was published in the Federal Register of June 21, 2000 (65 FR 38550).

The final rule establishing an exemption from the requirement of tolerance for residues of 1-methylcyclopropene in or on fruits and vegetables when used as a post harvest plant growth regulator, for the purpose of inhibiting the effects of ethylene, was approved and published in the Federal Register on July 26, 2002 (67 FR 48796).

## 1.3 Current applications of 1-MCP

1-methylcyclopropene (1-MCP) has been shown to specifically, and reversibly, suppress ethylene response and extend the postharvest shelf life and quality of several fruits and vegetables. In particular, climacteric fruits such as apple, tomato, and avocado are extremely responsive to 1-MCP (Huber et al., 2003).

1-MCP works by blocking the ethylene binding site (Serek et al., 1994). It was first utilized by the floral industry to keep flowers fresher longer (Reid et al., 2001).

It is sold for fruit as *SmartFresh*™ by AgroFresh, a division of Rohm and Haas; this is the sole commercial source of this compound (Sozzi and Beaudry, 2007).

1-MCP is formulated as a cyclodextrin powder. The cyclodextrin molecules form a soluble molecular "cage" that releases the 1-MCP gas molecules through aqueous dissolution (Blankenship and Dole, 2003).

1-MCP is currently available in four formulations from Agrofresh (Table 1.2). End-use products EthylBloc®, SmartFresh™, SmartTabs™ and EthylBloc™ sachets contain 0.14%, 3.3%, 0.63% and 0.014% of 1-MCP; respectively (U.S EPA, 2006).

Two delivery systems are available for use with fruits: tablets or sachets containing SmartFresh™ powder, sized to develop the appropriate treatment concentrations. When the product is mixed with water or a buffer solution, it releases the gas 1-MCP (Sozzi and Beaudry, 2007).

Current registration for use of SmartFresh™ exists in 27 countries and includes more than 24 different commodities including 23 fruit crops, of which 18 are tree fruits (Sozzi and Beaudry, 2007). The most common registrations are for apple (22 countries), avocado (13 countries), tomato (13 countries), and melon (9 countries). The number of tree fruit registrations is greatest for the USA (12), followed by Mexico (11).

Results obtained using 1-MCP in precommercial and commercial trials are sometimes accessible only to the sponsoring company or organization (Sozzi and Beaudry, 2007).

Table 1.2 Current products containing 1-MCP: Use site registration and registration date in the USA.

| Product name & Use sites | Registration date |
|---|---|
| Ethylbloc ®<br>Use Sites<br>Fresh cut flowers and potted flowering, bedding, nursery and foliage plants. | April 22, 1999 |
| SmartFresh ™<br>Use Sites<br>Post-harvest Fruits (apples, melons, tomatoes, pears, avocadoes, mangoes, papayas, kiwifruit, plums, apricots and persimmons | July 17, 2002 |
| SmartFresh ™ SmartTabs<br>Use Sites<br>food commodities derived from: apples, melons, tomatoes, pears, avocadoes, mangoes, papayas, kiwifruit, plums, apricots and persimmons | March 11, 2004 |
| Manufacturing Use Product SF | January 30, 2004 |
| Ethylbloc ® Sachet<br>Use Sites<br>Fresh cut flowers and potted flowering and foliage plants | February 3, 2006 |

Source: U.S EPA, 2006.

## 1.4 1-MCP benefits on tree fruits

The potential benefit of 1-MCP for different tree fruit crops is described in the literature (Table 1.3) in which respondents to an international survey ranked the potential benefit of 1-MCP use as (1) no known benefit to fair benefit, (2) good potential benefit, (3) very good potential benefit, or (4) excellent potential benefit.

Table 1.3 Summary of the potential benefit of 1-MCP on tree fruits.

| Potential benefit level | Tree fruit crop (score) |
|---|---|
| Excellent | Apple (3.92) |
| Very good | Persimmon (3.25)<br>Kiwifruit (3)<br>Plum (3)<br>Avocado (2.56)<br>European and Asia Pears (2.5) |
| Good | Mango (2.29)<br>Guava (2.20)<br>Papaya (2.20)<br>Banana and Plantain (2)<br>Cherimoya (2)<br>Loquat (2)<br>Peach and Nectarine (1.7) |
| Fair/no benefit | Pineapple (1.5)<br>Pomegranate (1.5)<br>Apricot (1.4)<br>Lime (1.4)<br>Berries (1)<br>Cherry (1)<br>Fig (1)<br>Grape (1)<br>Grapefruit (1)<br>Lemon (1)<br>Mandarin (1)<br>Orange (1) |
| Benefits not anticipated | Nuts and dried fruits - olive |

Adapted from Sozzi and Beaudry, 2007.

A summary of the most relevant potential benefits of 1-MCP to different tree fruits follows:

Apple (*Malus domestica*) was the first fruit to which 1-MCP could be applied and then sold for human consumption. The effect of 1-MCP on this crop has been widely studied in cultivars such as 'McIntosh', 'Empire', 'Delicious', 'Granny Smith', 'Fuji', 'Gala', etc. 1-MCP suppresses ethylene production and loss of tissue firmness in apples (Fan et al., 1999; Watkins et al., 2000; Reed, 2000). It also slows down the reduction in titratable acidity in most cultivars evaluated (Fan et al., 1999; Watkins et al., 2000; Reed 2000). The effect on total soluble solids is inconclusive because there have been reports that 1-MCP decreases (Watkins et al., 2000), increases (Fan et al. 1999) or has no effect (DeEll et al., 2002; Reed, 2002) on the total soluble solids of even the same cultivars. Treatment with 1-MCP reduced by 50% the volatile formation from Golden Delicious, Jonagold and Redchief Delicious fruit, relative to nontreated fruit, in a manner similar to CA storage (Ferenczi et al., 2006).

1-MCP delays avocado (*Persea americana*) ripening but renders it more susceptible to decay (Hoffman et al., 2000). Softening in several cultivars of avocado including Simmonds, Haas, Etinger, Reed and Fuerte was delayed by 1-MCP treatment through suppression of enzymes associated with the softening process (Feng et al., 2000; Jeong et al., 2002).

1-MCP treatment of bananas (*Musa acuminata*) can affect ethylene formation and respiration, volatile production, skin color, and pulp softening. Without exogenous ethylene, 1-MCP delays the onset of the climacteric stage

whereas in the presence of exogenous ethylene, it does not affect the onset of the climacteric, though treated fruit produce less ethylene and have a lower respiration rate (Golding et al., 1998). It also delays and reduces volatile production (Golding et al., 1999) and may induce uneven degreening (Jiang et al. 1999). 1-MCP treatment of mango (*Mangifera indica*) helps to maintain peel color and external appearance by preventing oxidation of skin pigments (Silva et al., 2004). 1-MCP treatment of papayas (*Carica papaya*) can effectively increase the time to ripen approximately 3-fold (Hofman et al., 2001).

On pears (*Pyrus communis*), 1-MCP mainly affects texture and ethylene production. The softening process in 'Barlett' pears that have started to ripen is slowed and completely inhibited in 'D'Anjou' pears (Baritelle et al., 2001; Calvo and Sozzy, 2004).

1-MCP slows the softening process in persimmon (*Dispyros kaki*) and reduces the production of off-flavor compounds, acetaldehyde and ethanol (Salvador et al., 2004).

1-MCP delays the ethylene and respiratory climacterics in plums (*Prunus domestica*) (Abdi et al., 1998; Salvador et al., 2003). Aroma production of 'Gulfruby' and 'Beauty' plums is arrested by 1-MCP but can be restored by propylene treatment (Abdi et al., 1998). It also reduces the production of off-flavor compounds (Salvador et al., 2003), and delays changes in skin color, softening and titratable acidity (Dong et al., 2002; Argenta et al., 2003; Valero et al., 2004).

## 1.5 Factors that determine the response to 1-MCP as a postharvest treatment

Success of fruit response to 1-MCP treatment depends on six main factors or sets of factors: (1) genotype (species and cultivar) and ripening physiology, (2) preharvest environmental conditions and practices, (3) harvest date (physiological age of fruit), (4) treatment conditions, (5) effect on susceptibility to pathological disorders, and (6) the postharvest environment (Sozzi and Beaudry, 2007).

The effect of treatment conditions (time, concentration, temperature) is described in the literature (Watkins, 2002; Blankenship and Dole, 2003). Responses are usually "concentration x exposure" dependent in fruits such as avocado, banana, guava, European pear, mango, peach and climacteric plums. Concentration of 1-MCP may be a limiting factor, because high concentrations can cause excessive delay in ripening or even prevent it, thus, selection of the appropriate concentration depends on the species and cultivar (Sozzi and Beaudry, 2007).

Indeed, findings from a study comparing 12 different fruits and vegetables (Nanthachai et al., 2007) suggests that the rate of sorption differs markedly (up to 30-fold) between species. Interestingly, the authors also determined that most of the 1-MCP applied must have been lost to one or more solid fractions of the plant material excluding the physiologically active binding site.

The possibility that 1-MCP is absorbed by one or more of the insoluble dry matter components suggests that materials that normally accompany

commodities inside refrigerated or controlled atmosphere facilities (treatment rooms) may absorb a significant portion of the 1-MCP during the exposure treatment time (Vallejo and Beaudry, 2006).

The loss of 1-MCP to non-target materials from fruit storage facilities was first described in the literature by testing the sorptive capacity of oak, plywood, high density polyethylene (HDPE) and polypropylene (PP) plastic bin material, corrugated board, urethane insulation and cellulose- based fire retardant, which are structural components of commercial treatment chambers (Vallejo and Beaudry, 2006). Findings from this study show large differences in absorption of 1-MCP by the different materials. Of the bin and box construction materials, those made from wood or wood fibre adsorbed significant quantities of 1-MCP while plastic bin material absorbed little to no 1-MCP. Urethane insulation and the fire retardant did not absorb 1-MCP. Importantly, wetting of the wood and corrugated board test samples dramatically increased absorption.

Probably, the most interesting result was related to a simulated CA storage treatment in which apple was placed in the treatment chamber alone; and in combination with a piece of wetted oak bin material. Inclusion of the wooden bin material caused the 1-MCP concentration to be depleted by half within the first 2 hours versus 12 hours if the wood was not included. The data suggested that the loss of 1-MCP to non-target materials commonly encountered in controlled atmosphere or regular atmosphere storage rooms is likely not of serious concern in situations when 1-MCP levels are near the maximum recommended rate (i.e. apple and pears). However, under sub-saturating

concentrations, significant sorption by fruit, or sorption by corrugated board or wood, might compromise 1-MCP efficacy (Vallejo and Beaudry, 2006).

Published data on headspace concentrations of 1-MCP in research or commercial treatment chambers is lacking; 1-MCP has been treated as relatively inert gas, the assumption being that when the material is added to an experimental chamber, a small portion of the applied gas is bound to the ethylene binding sites in the produce and the remainder of the material simply stays in the airspace of the treatment chamber until it is vented (Sozzi and Beaudry, 2007).

## 1.6 Conclusion

Traditionally, temperature and humidity control and modified atmospheres are used for fruits and vegetables to maintain quality and delay ripening and senescence. During the late 90's and beginning of this century, the use of compounds that specifically target and inhibit ethylene responsiveness have emerged as alternative technologies for delaying senescence and deterioration of perishable fruits, vegetables, potted plants, and cut flowers. 1-methylcyclopropene (1-MCP) suppresses ethylene response and extends the postharvest shelf life and quality of climacteric fruits. The impact of 1-MCP on the postharvest biology of climacteric fruits is well characterized; however, published data on the behavior of concentration of 1-MCP in the airspace of research and commercial treatment chambers is lacking.

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CHAPTER 2

# COMPARISON OF DIFFERENT PACKAGING MATERIALS IN CONCERT WITH 1–MCP IN DELAYING RIPENING OF BANANAS


***Abstract***

Corrugated board, low and high density polyethylene, and wood based packaging materials were compared for their effect on efficacy of 1-MCP in delaying ripening-associated processes such as changes in peel color and accumulation of $CO_2$ when applied to mature green, non-ripening, non-gassed banana fruits.

The data confirms that the effect of 1-MCP depends not only on initial 1-MCP concentrations in the atmosphere surrounding the fruit, but also on the type of packaging material used (corrugated board box, a Kraft paper pad, wood from pallets, plastic bins) in concert with the fruit at the time of treatment.

In general, concentrations of 1-MCP around 5-10 nL $L^{-1}$ were sufficient to suppress ripening and the accompanying increase in respiratory activity of the fruit which resulted in the accumulation of $CO_2$ in response to ethylene for fruit in treatment chambers in the absence of packaging materials. When corrugated board was present with the fruit at least 15 nL $L^{-1}$ of 1-MCP were needed to induce a similar magnitude of response. 1-MCP at concentrations of 5 nL $L^{-1}$ and 10 nL $L^{-1}$ suppressed the loss of green color in fruit packaged in corrugated high density polyethylene. However, the suppression of chlorophyll loss was marginal at 10 nL $L^{-1}$ and not evident at 5 nL $L^{-1}$ on fruit packed in corrugated board.

Concentrations of 1-MCP lower than 5 nL $L^{-1}$ occasionally induced uneven ripening and patchy loss of chlorophyll of fruit within the same treatment dose, whereas concentrations of 20 nL $L^{-1}$ were enough to completely block the response of fruit to ethylene even in the presence of the packaging materials tested.

In this test, the corrugated board significantly reduced the effectiveness of low doses of 1-MCP in delaying ripening-associated processes of the fruit in response to ethylene. The data suggest that current commercial recommendations should be amended to take into account the effect of sorption of 1-MCP by packaging materials.

## 2.1 Introduction

Traditionally manipulation of temperature, humidity and atmosphere has been used to maintain quality and delay over-ripening and senescence of fruits and vegetables.

During the last decade, the use of compounds that specifically target and inhibit ethylene responsiveness have emerged as technologies, which can be used to delay senescence and deterioration of perishable fruits, vegetables, potted plants, and cut flowers.

Ethylene is produced by all higher plants. It is known to induce ripening-associated processes such as softening, color change, conversion of starch to sugars, loss of acidity, etc, in climacteric fruits (Davies, 1995; Mauseth, 1991; Raven, 1992; Salisbury and Ross, 1992). Production of ethylene varies with the type of tissue, the plant species, and the stage of development. The mechanism by which ethylene is produced has been described (McKeon et al., 1995; Salisbury and Ross, 1992; Abeles et al., 1992).

1-methylcyclopropene (1-MCP) has been shown to specifically, and typically reversibly, suppress ethylene response and extend the postharvest shelf life and quality of several fruits and vegetables. In particular, climacteric fruits such as apple, tomato, and avocado are very responsive to 1-MCP (Huber et al., 2003).

1-MCP works by blocking the ethylene binding site, making it blind to the presence of ethylene (Serek et al., 1994). It was first utilized by the floral industry to keep flowers fresher longer (Reid et al., 2001).

1-MCP was discovered more than a decade ago, it is sold for fruit as *SmartFresh*™ by AgroFresh, a division of Rohm and Haas (the registrant company) and is formulated as a cyclodextrin powder that releases the gas through aqueous dissolution (Blankenship and Dole, 2003).

Definition of the problem

Currently, 1-MCP is used in commercial apple storage, as a complement to cold storage, for maintaining apple quality. A single exposure to 1-MCP can inhibit apple fruit sensitivity to ethylene, delay the rise in ethylene production and thus delay respiration, aroma production, and softening for more than 100-120 days for apples stored at 0°C (32°F) (Beaudry and Watkins, 2001).

In the United States and Canada, the label treatment dosage for apples is 1.0 and 0.6 μL $L^{-1}$, respectively. These dosages are recommended to supply 1-MCP at a concentration sufficient to saturate the response of the plant material (Pest Management Regulatory Agency, Health Canada, 2004).

However, saturating levels of 1-MCP (concentrations sufficiently high to completely block the ethylene receptors, thus inhibiting ethylene response) can cause excessive delay of ripening in some fruits, and alter ripening-related developmental processes sufficiently to significantly reduce product quality.

Thus, in some instances, it is preferable to obtain short-term or partial responses by using sub-saturating levels of 1-MCP (Calvo and Sozzi, 2004).

Golding et al. (1998) suggested that climacteric fruits might eventually make new receptors after 1-MCP treatment, allowing an active, normal, ethylene climacteric ripening response. This is more likely to occur for application situations in which the concentration of 1-MCP is not significantly above the minimal saturating concentration for a plant material, or for applications within the variable dose response range (Vallejo and Beaudry, 2006). In such circumstances, losses of 1-MCP during the exposure period might compromise the effectiveness of the product. Even assuming that the application is in a tight, sealed storage room (chamber or container) the presence of packaging materials (i.e. paperboard and/or corrugated paperboard) commonly used for commercial shipment of fruits, might have the ability to absorb 1-MCP from the storage environment, thereby reducing the effective concentration available for treatment. Vallejo and Beaudry (2006) demonstrated that wood and corrugated cardboard materials, commonly found in apple storage facilities, absorb 1-MCP.

Banana is a climacteric fruit, and as such shows marked physiological changes during ripening (Simmonds et al., 1987). Ripening is initiated by the natural evolution of endogenous ethylene as banana fruit reach full maturity. Commercially, an exogenous source of ethylene is used to induce and trigger endogenous production of ethylene while ensuring uniform ripening progression among fruit batches (Marriot, 1980).

Exposure to as little as 0.7 nL $L^{-1}$ of 1-MCP for 24 hours is required to protect bananas from the effects of ethylene for about 12 days at 25°C. After 12 days fruit responds to ethylene and resumes normal ripening (Sisler et al., 1998). Jiang et al. (1999) demonstrated that banana fruit ripening was delayed when exposed to 0.01 – 1.0 µL $L^{-1}$.

Non-published research conducted for a large multinational company showed that Gran Naine bananas treated with as low as 10 nL $L^{-1}$ of 1-MCP remained green after exposure to ethylene regardless of the ripening cycle used. Those results supplied the encouragement to do follow up experimentation in a range of concentrations near that level.

Because of the potential important implications on dosage recommendations of this phenomenon, a study was proposed to address the question of how packaging materials might compromise treatment dosages of 1-MCP for climacteric fruits. Bananas were used as the model system.

Objectives

1- Characterize and describe banana fruit responses to 1-MCP at concentrations near the minimal effective dosages when applied at the green stage in the presence of corrugated board, HDPE or wood, followed by treatment with ethylene.

2- Compare the effects of corrugated board, wood, and HDPE on 1-MCP sorption by determining the half-maximum effective concentration of applied 1-MCP.

## 2.2 Materials and Methods

### *2.2.1 BANANAS INDIVIDUALLY TREATED WITH 1-MCP IN 1.9 L GLASS JARS*

Fruit material:

A series of trials were conducted in 2006 at the Postharvest Technology and Physiology Laboratory in the Plant Sciences Building, MSU.

Mature green 'Gran Naine' bananas were obtained from the Detroit Terminal Market. The bananas used for these series of experiments were from Dole's commercial packs known as *150's*, which consist of 150 single fingers with the following specifications: length 17.8 to 20.3 cm, and caliper (width) 6 to 6.8 cm; packed in corrugated board cases weighing approximately 22.7 kg.

Fruit was collected every two weeks directly from inbound shipping containers to prevent contamination with ethylene from the ripening facilities and brought immediately to the laboratory. Fruit was harvested in farms located in Costa Rica, with a transit period from the tropics to the market estimated to be around 12 days.

Fruit was sorted to ensure freedom from visual defects and uniformity of weight and shape. Hue (H°) was measured (Minolta, CR-300, Japan) upon fruit arrival to the laboratory and the decrease in H° in response to treatment was measured.

Packaging materials tested included: HDPE specimens (1.2x11x1.8 cm), oak wood strips (7.2x11.4x0.5 cm) and corrugated board specimens (7.5x11.5x0.2 cm). Control fruit was tested in the absence of any packing

materials. The oak pieces were from commercial bins stored out-of-doors, and the HDPE specimens were from plastic bins (Macro Plastics, Fairfield, CA). The corrugated board was from commercial banana boxes with a combined basis weight of facings of 94 Lb per 1000 $ft^2$ (Packaging Corporation of America).

1-MCP:

1-MCP concentrations tested were 0, 0.5, 1, 2, 3, 4, 5, 10, 15, 20, 30, 40 and 60 nL $L^{-1}$. These were obtained from a concentrated source of 1-MCP (2000 µL $L^{-1}$) created by adding 10 mL of distilled water to a 0.47-L glass jar containing 0.064 g of *SmartFresh*™ (AgroFresh, Springhouse, PA), which had an active ingredient concentration of 3.3%. A fresh source of stock gas was prepared for each run.

The concentration of 1-MCP in the stock preparation was quantified by gas chromatography (Carle Series 100 AGC) using a 2 m (length) x 2 mm (inner diameter) stainless steel column packed with 60/80 Chromosorb OV-103 (Alltech Associates Inc., Deerfield, IL), and fitted with a flame ionization detector. The flow rates for the carrier gas (He), $H_2$, and air were approximately 50, 50 and 200 mL $min^{-1}$, respectively. The oven temperature was maintained at 140°C.

A 1-butene gas standard was used to determine the concentration of 1-MCP. To create a 10 µL $L^{-1}$ 1-butene standard, 43 µL of pure 1-butene (Matheson Gas Products, Chicago, IL), were injected into a 4.3 L specially-made glass chamber fitted with a Mininert valve (Supelco, Bellefonte, PA). It was assumed that the response factor for 1-MCP (molecular weight of 54.09 g/mol) and 1-butene (molecular weight of 51 g/mol) would be similar (Vallejo and

Beaudry, 2006). A standard curve for 1-butene was prepared for concentrations ranging between 1 to 10 μL $L^{-1}$, the relationship between 1-MCP and 1-butene was linear (Appendix A).

Experimental design:

One jar per concentration (C) and material type (M) was used, for a total of 52 jars per test run. The same experimental setup was repeated every other week for 20 consecutive weeks (total of 9 runs or replicates).

Upon fruit arrival to the laboratory; one banana finger, along with the corresponding treatment material, was placed into a 1.9-L glass Mason jar and closed with a metal lid fitted with rubber septa (Fisher Scientific, Springfield, NJ). A sufficient volume of the 1-MCP stock gas was added to the jar headspace to obtain a target 1-MCP gas concentration. A gas tight syringe was used to deliver the 1-MCP through the rubber septa. After 24 h the jars were vented with fresh air for 30 min and the HDPE, corrugated fiberboard and wood sticks were removed from the jars.

The fruit was then exposed to ethylene at an initial concentration of 50 μL $L^{-1}$ for 24 h at 20°C, by injecting ethylene gas (Matheson Gas Products, Chicago, IL) into the headspace of the jars, using a gas tight syringe.

The fruit were then removed from the jars and put into corrugated board boxes lined with HDPE (Muehlstein, Norwalk, CT) under ambient air conditions of ~20°C. The liner, with a thickness of $1.77 \times 10^{-5}$ m, had 36 perforations around the perimeter of the box, each having a diameter of 1.25 cm.

Fruit was evaluated daily for peel color. The scoring used for peel color was determined using a 1-7 commercial color scale (Dole color chart) described as follows: 1 = all green, 2 = light green, 3 = 50% green / 50% green yellow, 4 = more yellow than green, 5 = yellow with green tips, 6 = full yellow; and 7 = yellow flecked with brown.

When the control fruit had reached color stage 5, the peel H° of all bananas was measured (Minolta, CR-300, Japan). Each measurement was taken from three different points of the fruit peel (inner whorl, outer whorl and one side).

To measure the accumulation of $CO_2$ in the headspace of the jars, the banana fingers were placed back in the glass jars and sealed for 6 h prior to $CO_2$ sampling. A 100 µL gas sample was withdrawn by syringe and the sample injected into a $CO_2$ analyzer (ADC model 225-MK3, Hoddesdon, England) with nitrogen as the carrier gas.

To objectively determine the apparent, half-maximum effective concentration of 1-MCP applied, the relative amount of $CO_2$ formed for each treatment was fitted with an appropriate equation using commercial curve-fitting software (Table Curve 2D; Jandel Scientific, San Rafael, California).

Statistical significance was determined using analysis of variance and the software InfoStat Release 1.0 (Universidad Nacional de Cordoba, Argentina, 2001). Significant differences among treatment means was done using Fisher's least significant difference test at $P<0.1$.

### *2.2.2 BANANAS PACKAGED IN CORRUGATED HDPE VS. CORRUGATED PAPERBOARD BOXES AND TREATED WITH 1-MCP IN 114 L PLASTIC BARRELS*

After determining the 1-MCP dose responses, an experiment was designed using an increased sample size and a reduced number of 1-MCP concentrations. This was primarily a demonstration experiment to test whether the sorption by fiberboard had the potential to alter 1-MCP effectiveness under conditions more closely resembling commercial handling and packaging scenarios.

Treatments:

The treatments were as follows:

T1 - Fruit only, no added packing materials and no 1-MCP,

T2 - Fruit in corrugated fiberboard boxes and treated with 1-MCP at 5 nL $L^{-1}$,

T3 - Fruit in corrugated fiberboard boxes and treated with 1-MCP at 10 nL $L^{-1}$,

T4 - Fruit in corrugated plastic boxes and treated with 1-MCP at 5 nL $L^{-1}$, and

T5 - Fruit in corrugated plastic boxes and treated with 1-MCP at 10 nL $L^{-1}$.

Corrugated fiberboard boxes were the commercial "Quad-pack" Mini box type for Dole bananas with a combined basis weight of facings of 94 Lb per 1000 $ft^2$ (Packaging Corporation of America), taken from inbound shipping containers. Corrugated high density polyethylene (HDPE) boxes were assembled using a template of the "Quad-pack" mini box.

Fruit in both plastic and fiberboard boxes were packed using a HDPE liner (Muehlstein Inc., Norwalk, CT) with a thickness of $1.77 \times 10^{-5}$ m to protect bananas from mechanical injuries. Liners had approximately 36 perforations around its perimeter, each having a diameter of 1.25 cm. All boxes were filled to a total weight of 4.54 Kg of banana fruit with an average of 32 fingers per box.

Three boxes of each treatment were placed into different plastic barrels having a volume of 114-L with lids fitted with rubber septa (Fisher Scientific, Springfield, NJ) under ambient air conditions of ~20°C. Control fruit consisted of an equivalent weight of non-boxed fruit placed into plastic barrels. Each box was considered a replicate of the treatment. The same experimental setup was repeated two weeks after the first run.

Distilled water was added (3 L) to each barrel (chambers) to generate a relative humidity of 95% or greater in the airspace of the chambers. The relative humidity was measured using a moisture analyzer designed to operate with a dew point sensor (General Eastern, Model 8008). All boxes were placed empty into the chambers for 24 h prior to treatment with 1-MCP to ensure that they came to equilibrium with the relative humidity in the chambers.

Additionally, all plastic barrels, used as treatment chambers, were tested to determine their integrity by injecting a known concentration of 1-MCP in the headspace to obtain a target gas concentration of around 5 $\mu L\ L^{-1}$. Gas concentration in the headspace of the barrels was measured after 24 h. A slight declined of around 2% over the 24 h test period occurred suggesting that the barrels would maintain the desired concentration of 1-MCP.

Boxes were placed in a "cross-stacked" pattern. The barrel rims closures were coated with high vacuum grease (Dow Corning Corp., USA) to ensure proper gasket sealing. The fruit was then exposed to 1-MCP for 24 h at 20°C, and a sufficient volume of the 1-MCP stock gas was added to the headspace to obtain a target 1-MCP gas concentration. A gas tight syringe was used to deliver the 1-MCP through the rubber septa. A small fan powered with a lantern battery was placed inside each barrel to allow air flow through the boxes.

A concentrated source of 1-MCP (7,500 μL $L^{-1}$) was created by adding 10 mL of distilled water to a 0.47-L glass jar containing 0.32 g of SmartFresh (AgroFresh, Springhouse, PA), which had an active ingredient concentration of 3.3%. A fresh source of stock gas was prepared for each run. The actual concentration of 1-MCP in the stock preparation was quantified as previously described.

After 24 h, the barrels were opened and vented with fresh air for 30 min following treatment with 1-MCP. Fruit (with added packing materials) was subsequently exposed to ethylene at a concentration of 100 μL $L^{-1}$ for 24 h at 20°C. A single injection of pure ethylene gas (Matheson Gas Products, Chicago, IL) was delivered to the headspace of the barrels.

All boxes were removed from the barrels at the end of the 24 h exposure period and kept under ambient conditions at 20°C. Fruit was evaluated daily for peel color. The scoring used for peel color was determined using a 1-7 commercial color scale (Dole color chart) described as follows: 1 = all green, 2 =

light green, 3 = 50% green / 50% green yellow, 4 = more yellow than green, 5 = yellow with green tips, 6 = full yellow; and 7 = yellow flecked with brown.

When the control fruit reached color stage 5, the hue angle of all fingers from each treatment (N=96) was measured as previously described. Each measurement was taken from the center of the outer whorl of the banana finger. An initial H° was measured upon fruit arrival to the laboratory, and the subsequent decrease in H° represents a change in peel color from green to yellow.

For fruit from the second experimental lot, six randomly selected banana fingers per treatment were placed into 1.9-L glass Mason jars with metal lids fitted with rubber septa (Fisher Scientific, Springfield, NJ) and held at a constant temperature of 20°C for 6 h. The accumulation of $CO_2$ was measured on a 100-µL sample withdrawn using a syringe and analyzed using a $CO_2$ analyzer (ADC model 225-MK3, Hoddesdon, England) with nitrogen as the carrier gas. The respiration rate was calculated based on the $CO_2$ accumulation rate using the following relationship: Respiration rate = ($CO_2$ % / 100) x ($V_{total}$ in mL / sample weight in Kg) x (1 / t in hours)

This experiment was repeated once and for each run banana fingers were sampled from different replicates (boxes). Statistical significance was determined using analysis of variance and the software InfoStat Release 1.0 (Universidad Nacional de Cordoba, Argentina, 2001). Significant differences among treatment means were determined using Fisher's least significant difference test at $P<0.1$.

## 2.3 Results and Discussion

### *2.3.1 BANANA FINGERS INDIVIDUALLY TREATED WITH 1-MCP IN 1.9 L GLASS JARS*

Four days after application with ethylene, control fruit without 1-MCP reached color stage 5. At that time the accumulation of CO2 in the headspace of the jars was measured, results are summarized in Table 2.1. Treatments within columns with the same letter are not statistically different at 1% level (FLSD), each value is the average of 7 determinations on a single fruit samples each time.

Changes in the percent $CO_2$ in the jars depended on 1-MCP dosage concentration and the type of packing material present in the jars. In general, concentrations of 1-MCP greater than 10 nL $L^{-1}$ prevented an increased (a 50% reduction or more) in the respiratory climacteric of the fruit. When corrugated board was present, at least 15 nL $L^{-1}$ of 1-MCP were needed to induce a similar magnitude of response. There was no difference between treatments at 1-MCP concentrations greater than 15 nL $L^{-1}$.

Table 2.1 Percent (%) $CO_2$ accumulated in 1.9 L glass jars after enclosing fruit for 6 hr with and without packing materials.

| | $CO_2$ (%) | | | |
|---|---|---|---|---|
| 1-MCP (ppb) | Control | Plastic | Wood | CB |
| 0 | 3.95 d | 4.62 e | 4.8 c | 4.14 c |
| 0.5 | 4.12 d | 4.31 de | 4.63 c | 5.01 c |
| 1 | 4.23 d | 4.54 e | 3.96 c | 4.94 c |
| 2 | 4.18 d | 3.91 cde | 3.92 c | 4.56 c |
| 3 | 2.47 c | 3.07 bc | 2.41 b | 4.16 c |
| 4 | 2.56 c | 3.2 bcd | 2.66 b | 4.07 bc |
| 5 | 2.47 c | 2.56 b | 2.65 b | 4.3 c |
| 10 | 1.74 bc | 1.27 a | 2.29 b | 3.15 b |
| 15 | 0.7 ab | 0.7 a | 0.65 a | 1.61 a |
| 20 | 0.74 ab | 0.68 a | 0.68 a | 0.7 a |
| 30 | 0.61 a | 0.82 a | 0.85 a | 0.84 a |
| 40 | 0.86 ab | 0.81 a | 0.85 a | 0.76 a |
| 60 | 0.8 ab | 0.72 a | 0.82 a | 0.65 a |

The data describing the increase in $CO_2$ could be empirically fit by several of the equations provided by the curve-fitting software. Of these, those equations having constants that could be used to gather physiologically relevant data such as maximum effective concentration of 1-MCP were evaluated further.

Of these, the equation providing the best fit for all treatment profiles was: *y=a+0.5b(1+erf((logx-c)/(2^(0.5)d)))*, where *x* is the applied concentration of 1-MCP, *erf* computes the error function of *x*, *y* is the estimated percentage of $CO_2$, and *a*, *b*, *c* and *d* are constants.

The value of *c* was used to obtain an objective estimate of the half-maximum effective concentration of 1-MCP ($D_{50}$) required to reduce the respiratory activity of the fruit ($D_{50} = 10^C$). The relationship between *a*, *b* and *d* and curve shape was not evident.

The apparent half-maximum effective concentration of the 1-MCP applied to the control fruit was 3.83 nL $L^{-1}$; while for plastic and wood the half-maximum effective concentrations were 4.61 and 3.72 nL $L^{-1}$. The half-maximum effective concentration of 1-MCP was doubled due to the effect of corrugated board on the effective concentration of 1-MCP applied to the fruit (Table 2.2).

These results are further illustrated in figure 2.1. Each value shown is the average of 6 determinations on a single fruit samples. Vertical lines represent standard deviation, and are only shown for control fruit (no packing materials) for clarity (variation for all other treatments was similar).

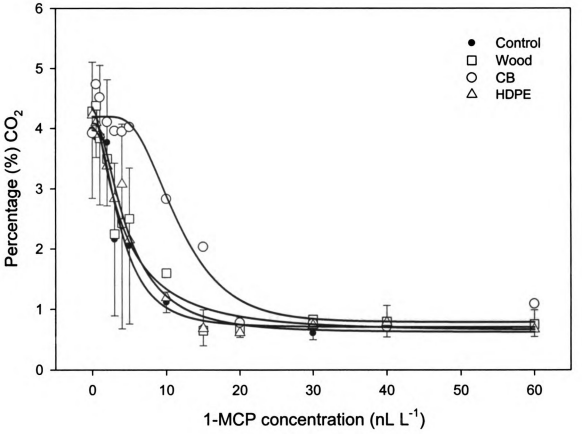


Figure 2.1 Percent (%) $CO_2$ accumulation in 1.9 L glass jars after enclosing fruit for 6 hr with and without packing materials.

Table 2.2 Constants *a*, *b*, *c*, and *d* and coefficient of determination for fit of $CO_2$ data from Gran Naine bananas treated with 1-MCP at concentrations between 5-60 nL $L^{-1}$, with subsequent exposure to ethylene for 24 h at 20°C.

| | Values for constants | | | | | |
|---|---|---|---|---|---|---|
| Treatments | a | b | c | d | $R^2$ | $D_{50}$ |
| Control | 0.706 | 3.266 | 0.583 | -0.322 | 0.97 | 3.83 a |
| HDPE | 0.625 | 3.462 | 0.663 | -0.354 | 0.98 | 4.61 a |
| Wood | 0.647 | 3.708 | 0.571 | -0.479 | 0.97 | 3.72 a |
| CB | 0.789 | 3.407 | 1.057 | -0.196 | 0.97 | 11.40 b |

Treatments with the same letter (within column showing $D_{50}$ values) are not statistically different at 1% level (FLSD).

Four days after application with ethylene, control fruit without 1-MCP reached color stage 5. At that time all fingers from each treatment were measured for their peel Hue angle (H°) using a colorimeter (Minolta, CR-300, Japan). A decrease in H° represents a change in peel color from green to yellow.

Results from the H° analysis are summarized in Table 2.3. Treatments within columns with the same letter are not statistically different at 1% level (FLSD). Color 1 on the commercial scale corresponds to an H° of approximately 120° for each lot of fruit; color 5 corresponds to an H° of approximately 91°. Each number represents the average of 6 determinations, for a single fruit sample.

Changes in peel color (hue angle) not only depended on 1-MCP concentrations, but also on the type of material present with the fruit in the jars (Table 2.3). In general, it was observed that concentrations of 1-MCP lower than 5 nL $L^{-1}$ occasionally induced uneven ripening and patchy loss of chlorophyll of fruit within the same treatment dose (data not shown). Concentrations of at least

10 nL $L^{-1}$ of 1-MCP were needed to significantly reduce (a 50% reduction or more) fruit response to ethylene for control fruit and fruit with plastic or wood. For fruit with corrugated board, concentrations of at least 15 nL $L^{-1}$ of 1-MCP were needed to suppress fruit response to ethylene, while concentrations of 20 nL $L^{-1}$ were enough to completely block the response of fruit to ethylene even in the presence of the packaging materials tested. In this test, the corrugated board in the presence of the fruit showed the most significant effect in reducing the 1-MCP available for delaying peel color change in response to ethylene.

Table 2.3 Degree of reduction in the Hue angle (H°) from its initial value of 120 at color stage 1, to when control fruit reached color grade 5.

| | ΔºH | | | |
|---|---|---|---|---|
| 1-MCP (nL $L^{-1}$) | Fruit Only | Fruit + Plastic | Fruit + Wood | Fruit + CB |
| 0 | 27.07 e | 27.74 d | 26.91 c | 27 d |
| 0.5 | 26.35 e | 26.77 cd | 27.01 c | 26.22 d |
| 1 | 23.16 de | 26.31 cd | 27.18 c | 27.14 d |
| 2 | 25.51 de | 20.19 bcd | 22.55 c | 26.78 d |
| 3 | 22.54 de | 18.34 bc | 22.5 c | 26.43 d |
| 4 | 21.41 cde | 21.52 bcd | 21.04 c | 26.37 d |
| 5 | 17.71 cd | 17.09 b | 20.53 c | 26.36 d |
| 10 | 13.33 bc | 12.78 ab | 12.38 b | 19.84 cd |
| 15 | 9.2 ab | 8.19 a | 7.89 ab | 13.79 bc |
| 20 | 5.66 ab | 6.69 a | 6.36 ab | 9.79 ab |
| 30 | 4.13 a | 6.09 a | 3.78 a | 9.48 ab |
| 40 | 3.51 a | 4.87 a | 4.62 ab | 5.14 a |
| 60 | 4.01 a | 4.65 a | 4.35 ab | 4.03 a |

The data describing the decrease in H° could be empirically fit by several of the equations as described before. The equation providing the best fit for all treatment profiles was: *y=a+0.5b(1+erf((logx-c)/(2^(0.5)d)))*, where *x* is the applied concentration of 1-MCP, *erf* computes the error function of *x*, *y* is the estimated change in H°, and *a*, *b*, *c* and *d* are constants.

The value of *c* was used to obtain an objective estimate of the half-maximum effective concentration of 1-MCP ($D_{50}$) required to reduce the change in peel color ($D_{50} = 10^{C}$). The relationship between *a*, *b* and *d* and curve shape was not evident.

The apparent half-maximum effective concentration of the 1-MCP applied to the control fruit was 8.13 nL $L^{-1}$; while for plastic and wood the half-maximum effective concentrations were 6.25 and 7.46 nL $L^{-1}$. The half-maximum effective concentration of 1-MCP was increased by nearly 50% due to the effect of corrugated board on the effective concentration of 1-MCP applied to the fruit. However, results from Fisher's LSD test suggest that those differences were minimal and not significant (Table 2.4).

These results are further illustrated in figure 2.2. Each value shown is the average of 6 determinations on a single fruit samples. Vertical lines represent standard deviation and are only shown for control fruit (no packing materials) for clarity (variation for all other treatments was similar).

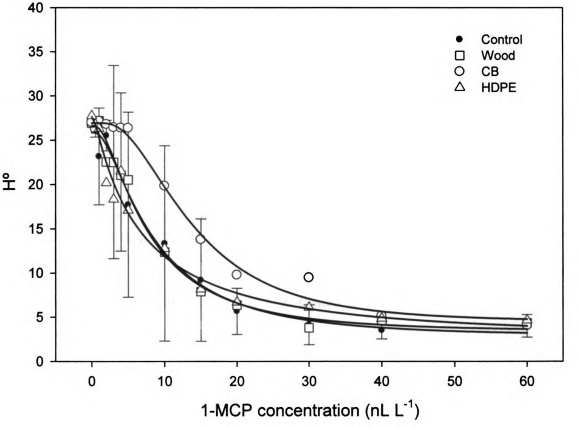


Figure 2.2 Reduction in Hue angle from its initial value of approximately 120°H at color stage 1 of Gran Naine bananas treated with 1-MCP at concentrations between 5-60 nL $L^{-1}$.

Table 2.4 Constants *a*, *b*, *c*, and *d* and coefficient of determination for fit of H° data from Gran Naine bananas treated with 1-MCP at concentrations between 5-60 nL $L^{-1}$, with subsequent exposure to ethylene for 24 h at 20°C.

| | Values for constants | | | | | |
|---|---|---|---|---|---|---|
| Treatments | a | b | c | d | $R^2$ | $D_{50}$ |
| Control | 2.874 | 22.998 | 0.910 | -0.397 | 0.99 | 8.13 a |
| HDPE | 2.695 | 24.943 | 0.796 | -0.605 | 0.97 | 6.25 a |
| Wood | 3.395 | 23.227 | 0.873 | -0.393 | 0.99 | 7.46 a |
| CB | 4.491 | 22.441 | 1.133 | -0.287 | 0.99 | 13.58 a |

Treatments with the same letter (within column showing $D_{50}$ values) are not statistically different at 1% level (FLSD).

The inability of Fisher's LSD test to detect differences between treatment means for $D_{50}$ of H° data might be due to the large fruit-to-fruit variability observed in the response of banana to 1-MCP within each treatment/concentration combination. This variability reflects commercial reality in terms of variability of product and suggests that the results must be interpreted with caution. Considering that fruit was collected at different times over a period of several weeks, some experimental variability due to naturally occurring differences between fruit batches was expected.

The physiological stage of the fruit at the moment of harvest, number of days from harvest to application of ethylene, environmental conditions during harvesting, temperature fluctuations during transit, handling, and warehousing

condition, can all influence/alter the ripening behavior of the fruit, and therefore affect its sensitivity to both ethylene and 1-MCP.

To reduce biological variability among fruit batches, fruit at the same harvest age, same farm location, and season of the year could be selected. Such a protocol could probably be met if the research was done directly in the tropics. A local alternative at MSU could be to increase the sample size and reduce the number of treatments by selecting the ones with more promising results.

After identifying the range of 1-MCP concentrations that yielded sub-saturating responses, the next step was to pack sample size boxes containing about 4.5 Kg of fruit and then to select only those 1-MCP concentrations that, if reduced slightly by non target materials, would yield a marked change in response.

### *2.3.2 BANANAS PACKAGED IN CORRUGATED HDPE VS. CORRUGATED FIBERBOARD BOXES AND TREATED WITH 1-MCP IN 114 L PLASTIC BARRELS*

Control fruit exhibited the expected response to ethylene, and underwent an extensive change in peel color, reaching color stage 5 (full yellow with green tips) five days after treatment with ethylene (Figure 2.3). Color progression for fruit treated with 1-MCP at concentrations of 5 nL $L^{-1}$ and 10 nL $L^{-1}$ was clearly influenced by the type of packaging material used during the exposure to 1-MCP: treatment of fruit in plastic boxes with 1-MCP prevented peel color change at both concentrations tested, but if the boxes were made of corrugated board, the suppression of color change by 1-MCP was largely relieved (Figure 2.3).

Fruit in corrugated board boxes exhibited uneven ripening and patchiness (data not shown). The effect of 1-MCP treatment was greater for fruit treated at a concentration of 10 nL $L^{-1}$ which suggests that corrugated board absorbed sufficient 1-MCP from the atmosphere to reduce its effects on the fruit.

No significant differences were detected between fruit in plastic boxes treated with 1-MCP at 5 nL $L^{-1}$ and 10 nL $L^{-1}$, suggesting that concentrations as low as 5 nL $L^{-1}$ are enough to inhibit peel color changes when fruit is packaged in HDPE, and that any interaction between polyethylene based materials and 1-MCP is minimal and not significant.

In Figure 2.3, each value is the average of 96 individual readings taken per treatment, vertical lines around each value represent the standard deviations. Treatments with the same letter are not statistically different at 1% level (FLSD).

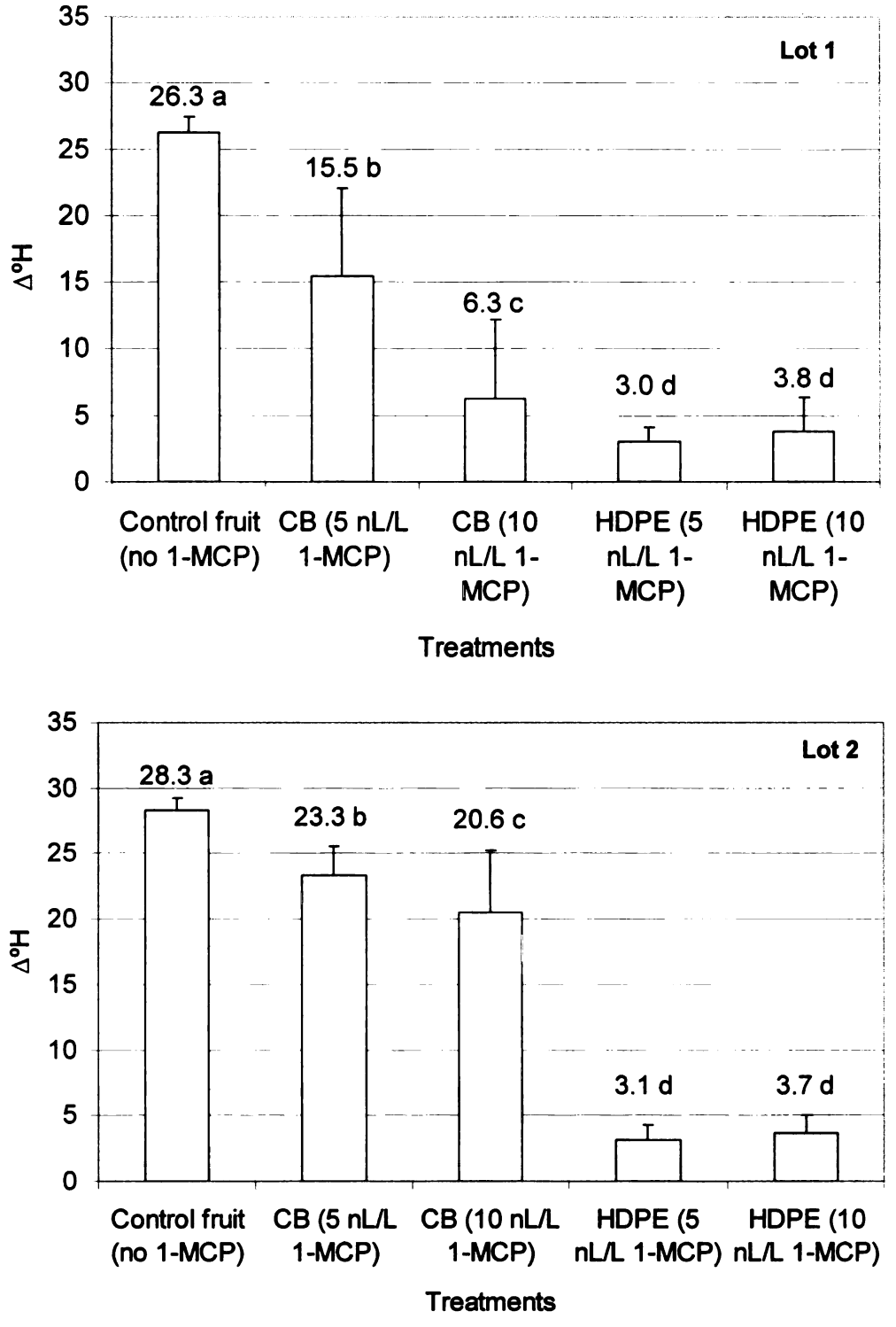


Figure 2.3 Reduction in hue angle (ºH) in Gran Naine bananas from an initial value of approximately 120ºH at color stage 1 as a function of 1-MCP treatment and package composition on 2 lots of fruit.

After ripening to color stage 5 following induction by ethylene, control fruit respiration was approximately 140 mL $CO_2$ / kg.h. Treatment with either 5 or 10 nL $L^{-1}$ of 1-MCP prevented rise in fruit respiration in the plastic boxes such that respiration was approximately 18 mL $CO_2$ / kg.h, whereas corrugated board fruit respiration was approximately 130 mL $CO_2$ / kg.h (Figure 2.4). The respiration rates obtained for both yellow and green bananas are consistent with previous findings (Kader, 2007).

Consistent with previous results on $CO_2$ production by the individual fingers in the glass jars, changes observed in respiration rates upon application of ethylene depended not only on 1-MCP dosage concentration but also on the type of material from which boxes were made (Figure 2.4). In general, concentrations as low as 5 nL $L^{-1}$ of 1-MCP were enough to prevent climacteric rise activity of fruit packaged in plastic boxes. This confirms that this type of plastic material does not absorb appreciable amounts of 1-MCP from its surrounding atmosphere.

However, at these same 1-MCP dosages, corrugated board seemed to absorb 1-MCP from the atmosphere, and reduced its availability to the fruit packed in these boxes.

Treatments with the same letter are not statistically different at 1% level (FLSD). Measurements began when control fruit had reached color stage 5. Each value is the average of 6 separate jars (N=6 fruits), and vertical lines represent the standard deviation of each calculated value.

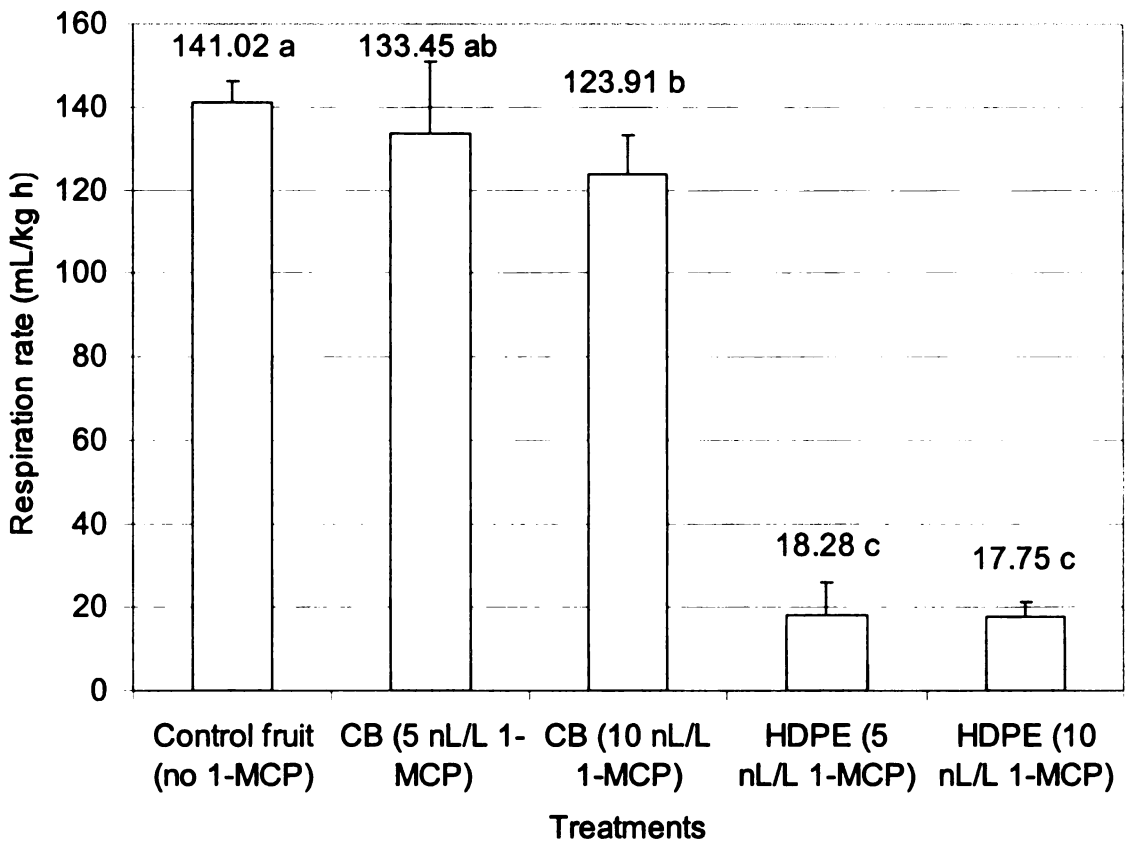


Figure 2.4 Respiration rates as $CO_2$ production (mL/kg.h) inside 1.9 L glass jars after enclosing fruit for 6 hr.

Respiratory activity can be extrapolated to the ripening behavior of fruit: 1-MCP retarded ripening, and the plastic material did not interfere with 1-MCP action on the fruit, while corrugated fiberboard significantly reduced the actively amount of 1-MCP in the atmosphere surrounding the fruit.

## 2.4 Conclusion

The data confirm that part per billion levels of 1-MCP delays ripening-associated processes such as change in peel color. Respiration rates depend not only on initial 1-MCP concentrations in the atmosphere surrounding the fruit but also on factors affecting 1-MCP concentration during treatment like the type of packaging material present with the fruit at the time of treatment, whether a corrugated board box, a Kraft paper pad, wood from pallets where fruit boxes are stacked, etc.

Findings from this study suggest that corrugated board alters the dose response because it absorbs some of the 1-MCP present, thus reducing the effectiveness of low doses of 1-MCP. Polyethylene based (HDPE and LDPE) materials absorb very little 1-MCP.

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CHAPTER 3

# COMPARISON OF CORRUGATED BOARD, HDPE, AND WOOD RELATIVE TO THEIR EFFECT ON THE AVAILABLE CONCENTRATION OF 1-MCP OVER A PERIOD OF TIME OF 24 H AT 21°C AND RELATIVE HUMIDITIES OF 50%, 80% and >95%


## *Abstract*

Corrugated board, high density polyethylene (HDPE), and wood (*Gmelina arboreus*) materials were included in a study to determine their effect on the available concentration of gaseous 1-methylcyclopropene (1-MCP) in an enclosed chamber.

The materials were evaluated individually in sealed treatment chambers under conditions of 21°C and relative humidities of 50%, 80%, and >95%. 1-MCP gas was added to the headspace at concentrations of 10 and 20 μL $L^{-1}$. Gas concentrations were measured every hour during the first 6 hours of the experiment, then every 3 hours during the following 6 hours and then every 6 hours until a 24 hour treatment period was completed.

The concentration of 1-MCP declined in the presence of the materials tested, but the rate at which 1-MCP gas was removed from the chamber headspace differed markedly. The average percentage loss for HDPE and wood was between 10-12% at all conditions tested, while for corrugated fiberboard it ranged from 12% to 94%.

The concentration of 1-MCP at any time *t* seems to follow a decrease behavior that can be fitted by the exponential model $C_t = C_0e^{-kt}$ where $C_t$ is the

concentration of 1-MCP at any time *t*, $C_0$ is the initial concentration of 1-MCP, *e* is the base of the natural logarithm, and *k* is a constant related to the rate at which 1-MCP gas is removed from the chamber headspace.

In the presence of corrugated fiberboard, and as the relative humidity increased from 50% to 80%, the value of the constant *k* (related to the rate at which 1-MCP gas was removed from the chamber headspace) increased up to 10-fold. As humidity increased further to 95%, a slight decrease was observed. The value of the constant *k* doubled as the ratio of material was increased from 4 to 8 kg of corrugated fiberboard / $m^3$ air. An increase of initial concentration from 10 to 20 μL $L^{-1}$ reduced by half the value of the constant *k*. This trend was also observed in the presence of HDPE based materials.

The loss of 1-MCP in the presence of corrugated board occurred more readily during the first 9 hours of the treatment period. The mechanism for this behavior is not yet known, however, transport properties of paper and paperboard are known to be inherently related to the resistance offered by the three dimensional structure of paper materials, and are likely affected by characteristics such as porosity, fiber-void interfacial area (surface area), pore size distribution, and structural tortuosity.

## 3.1 Introduction

The loss of 1-MCP to non-target materials normally encountered in fruit storage facilities was first described in the literature by testing the sorptive capacity of oak, plywood, high density polyethylene (HDPE) and polypropylene (PP) plastic bin material, corrugated board, urethane insulation and cellulose-based fire retardant (Vallejo and Beaudry, 2006).

Findings from this study show large differences in absorption of 1-MCP by the different materials. Of the bin and box construction materials, those made from wood or wood fiber adsorbed significant quantities of 1-MCP while plastic bin material absorbed little to no 1-MCP. Urethane insulation and the fire retardant did not absorb 1-MCP. Importantly, wood and corrugated board test samples dramatically increased depletion of 1-MCP in the test chambers.

Published data on headspace concentrations of 1-MCP in the airspace in research or commercial treatment chambers is lacking; 1-MCP has been treated as relatively an inert gas, the assumption being that when the material is added to an experimental chamber, a small portion of the applied gas is bound to the ethylene binding sites in the produce and the remainder of the material simply stays in the airspace of the treatment chamber until it is vented (Sozzi and Beaudry, 2007).

A series of tests were conducted to evaluate the effect of corrugated board, wood and HDPE in side-by-side tests, in a controlled temperature environment of 20°C and various relative humidities ranging between 50% to

saturation (~100%) on concentration of 1-MCP. The objectives of this study are presented as follows.

Objectives

1- Characterize the effect (if any) of wood, high density polyethylene (HDPE), and corrugated board on the concentration of 1-MCP during a treatment period of 24 hours.

2- Evaluate the effect (if any) of the amount of packaging material in the treatment chamber on the change from initial concentration of 1-MCP during a treatment period of 24 hours.

3- Determine the effect (if any) of concentration of 1-MCP on the effective dose available in the treatment chamber in the presence of wood, high density polyethylene (HDPE), and corrugated board during a treatment period of 24 hours.

4- Compare the effect (if any) of different relative humidities on availability of 1-MCP when applied in sealed chambers in the presence of wood, high density polyethylene (HDPE), and corrugated board during a treatment period of 24 hours.

5- Determine how long it takes for packaging materials to absorb 1-MCP.

## 3.2 Materials and Methods

### *3.2.1 Preliminary characterization of wood, high density polyethylene (HDPE), and corrugated board and their effect on the concentration of 1-MCP.*

Packaging materials

A series of experiments were conducted to evaluate the effect of different materials on the stability of 1-MCP during a treatment period of 24 hours.

Packaging materials tested included: HDPE specimens (1.2x11 cm, thickness of ~$1.77x10^{-5}$ m), wood (*Gmelina arboreus*) cubes (1.5x1.5x1.5 cm) and corrugated board specimens (7.5x11.5x0.2 cm). Control was an empty jar tested in the absence of any packing materials. The melina wood pieces were taken from commercial pallets stored in a ripening facility, the HDPE was taken from a commercial plastic liner used to pack bananas (Muehlstein Inc., Norwalk, CT), the corrugated board was taken from banana boxes having a combined basis weight of facings of 94 Lb per 1000 $ft^2$ (Packaging Corporation of America).

Materials were conditioned at standard conditions of 20°C, 50% RH for 72 hours to ensure that were in equilibrium. In addition, a condition of 20°C, 80% RH was included to evaluate the effect of higher RH. To ensure that these conditions were established and maintained during the experiments, room 125 and one of the conditioning chambers in room 124 of the Packaging Building were used.

Samples were weighed at the beginning and at the end of the testing period. The moisture content was determined by drying the corrugated board and wood samples in an oven at 105 °C for 1 hour, and then cooled in a dry

environment and then re-weighed (according to American Society for Testing and Materials - ASTM D644). The moisture content of wood and corrugated board was calculated on a dry weight basis and on a wet weight basis, respectively.

1-MCP

The 1-MCP concentration used in these tests was 20 μL $L^{-1}$. It was obtained from a concentrated source of 1-MCP (2000 μL $L^{-1}$) created by adding 10 ml of distilled water to a 0.47 L glass jar containing 0.064 g of *SmartFresh*™ (AgroFresh, Springhouse, PA), which had an active ingredient concentration of 3.3%.

The concentration of 1-MCP in the stock preparation was quantified using gas chromatography (Carle Series 100 AGC) using a 2 m (length) x 2 mm (inner diameter) column packed with 60/80 Chromosorb OV-103 (Alltech Associates Inc., Deerfield, IL), and fitted with a flame ionization detector. The flow rates for the carrier gas (He), $H_2$, and air were approximately 50, 50, and 200 ml $min^{-1}$, respectively. The oven temperature was maintained at 140°C.

A 1-butene gas standard was used to corroborate the concentration of 1-MCP. To create a 10 μL $L^{-1}$ 1-butene standard, 43 μL of pure 1-butene (Matheson Gas Products, Chicago, IL), was injected into a 4.3 L specially-made glass chamber fitted with a Mininert valve (Supelco, Bellefonte, PA).

It was assumed that the response factor for 1-MCP (molecular weight of 54.09 g/mol) and 1-butene (molecular weight of 51 g/mol) would be similar. A standard curve for 1-butene was prepared for a concentrations ranging between

1 to 10 μL $L^{-1}$, the relationship between 1-MCP and 1-butene was linear (Appendix A).

Effect of material type on depletion of 1-MCP

The sample materials were placed into 1-L glass Mason jars with metal lids fitted with rubber septa (Fisher Scientific, Springfield, NJ), 3 jars per treatment (N=24) were included in the test. The amount of material added to each chamber headspace was 2 g of HDPE, 6 g of corrugated board and 14 g of wood.

A sufficient volume of the 1-MCP stock gas was injected into treatment jars with a headspace volume of 1 L to obtain a target 1-MCP gas concentration of around 20 μL $L^{-1}$. Gas concentrations in the headspace of the treatment jars were measured after 0, 3, 6, 9, 12, and 24 h. The concentration of 1-MCP in the airspace of the treatment chambers was measured on a 1000 μL sample withdrawn by syringe and analyzed using gas chromatography.

Statistical significance was determined using analysis of variance and the software InfoStat Release 1.0 (Universidad Nacional de Cordoba, Argentina, 2001). Significant differences among treatment means was done using Fisher's Least Significant Difference Test at $P<0.1$.

*3.2.2 Evaluation of the effect of relative humidity, amount of packaging material in the treatment chamber, and initial concentration on availability of 1-MCP.*

After identifying the materials that seemed to have a significant effect on the availability of 1-MCP, the next step was to increase sample size and treatment chamber volume. The treatments used are shown in table 3.1.

Table 3.1 Treatments used to test the effects of relative humidity, amount of packaging material in the treatment chamber, and initial concentration on availability of 1-MCP.

| Relative Humidity | Amount of corrugated fiberboard and HDPE: kg of material/$m^3$ air space | 1-MCP (initial concentration) |
|---|---|---|
| 50, 80, 95% | 4 | 10 $\mu L\ L^{-1}$ |
| 50, 80, 95% | 8 | 10 $\mu L\ L^{-1}$ |
| 50, 80, 95% | 4 | 20 $\mu L\ L^{-1}$ |
| 50, 80, 95% | 8 | 20 $\mu L\ L^{-1}$ |

Corrugated board boxes were the commercial "Quad-pack" mini box type (Dole bananas) with a combined basis weight of facings of 94 Lb per 1000 $ft^2$ (Packaging Corporation of America). Corrugated HDPE boxes were assembled using a template of the "Quad-pack" mini box type.

The boxes were placed empty in plastic barrels having a volume of 114 L with lids fitted with rubber septa (Fisher Scientific, Springfield, NJ) and conditioned for 24 h prior to treatment with 1-MCP. The ratio of mass of packaging material (kg) per unit volume ($m^3$) of airspace of the treatment

chamber was selected to mimic average conditions in commercial forced-air ripening rooms.

Aqueous salt solutions were prepared with distilled water and chemically pure salts of magnesium nitrate and sodium chloride were used to generate the desired relative humidities of 50% and 80%, respectively, in the airspace of the chambers. The relative humidity was measured using a moisture analyzer designed to operate with a dew point sensor (General Eastern, Model 8008).

Additionally, all plastic barrels used as treatment chambers were previously tested for their seal integrity by injecting a known concentration of 1-MCP in the headspace to obtain a target gas concentration of around 5 $\mu L\ L^{-1}$. Gas concentrations in the headspace of the barrels were measured after 24 h. The headspace levels of 1-MCP declined by ~2% over the 24 h test period suggesting that the barrels would function as a stable treatment chamber.

A concentrated source of 1-MCP (7,500 $\mu L\ L^{-1}$) was created by adding 10 ml of distilled water to a 0.47-l glass jar containing 0.32 g of Smart-Fresh (AgroFresh, Springhouse, PA), which had an active ingredient concentration of 3.3%. A fresh source of stock gas was prepared for each set of experiments.

A 1-butene gas standard was used to calculate the concentration of 1-MCP. To create a 10 $\mu L\ L^{-1}$ 1-butene standard, 43 µL of pure 1-butene (Matheson Gas Products, Chicago, IL), was injected into a 4.3-L specially made glass chamber fitted with a Mininert valve (Supelco, Bellefonte, PA). It was assumed that the response factor for 1-MCP and 1-butene were similar (Vallejo and Beaudry, 2006). A standard curve for 1-butene was prepared for

concentrations ranging between 1 to 10 μL $L^{-1}$, the relationship between 1-MCP and 1-butene was linear (Appendix A)..

The concentration of 1-MCP in the stock preparation was quantified by gas chromatography (Carle Series 100 AGC) using an oven temperature of 140°C, a 2 m (length) x 2 mm (inner diameter) stainless steel column packed with 60/80 Chromosorb OV-103 (Alltech Associates Inc., Deerfield, IL), and fitted with a flame ionization detector. The flow rates for the carrier gas (He), $H_2$, and air were approximately 50, 50 and 200 ml $min^{-1}$, respectively.

Plastic tubing was used to connect the concentrated 1-MCP source container to a water reservoir. As the gas was removed from the 1-MCP source container, that same volume was replaced with water from the reservoir, thereby preventing dilution of the 1-MCP source or the creation of a pressure deficit.

Boxes were placed in a "cross-stacked" pattern. Barrel closure edges were coated with high vacuum grease (Dow Corning Corp., USA) to ensure proper gasket sealing. The material was then exposed to 1-MCP for 24 h at 20°C, a sufficient volume of the 1-MCP stock gas was added to the headspace to obtain a target 1-MCP gas concentration. A gas tight syringe was used to deliver the 1-MCP through rubber septa.

The concentration of 1-MCP in the airspace of the treatment chambers was measured on a 1000 μL sample withdrawn by syringe and analyzed using gas chromatography. Samples were taken every hour during the first 6 hours of the experiment, then every 3 hours during the following 6 hours, and then every 6 hours until a 24 hour treatment period was completed.

## 3.3 Results & Discussion

### *3.3.1 Preliminary characterization of wood, high density polyethylene (HDPE), and corrugated board and their effect on the concentration of 1-MCP.*

Figure 3.1 shows the results for the different materials at conditions of 20°C and 50% RH. In general, the concentration of 1-MCP decreased slightly for all treatment chambers at a similar rate regardless of the type of material tested. After 24 hours the initial concentration of 1-MCP had declined by about 11% as an average for all treatments. Each value is the average of three determinations. Vertical lines represent standard deviation.

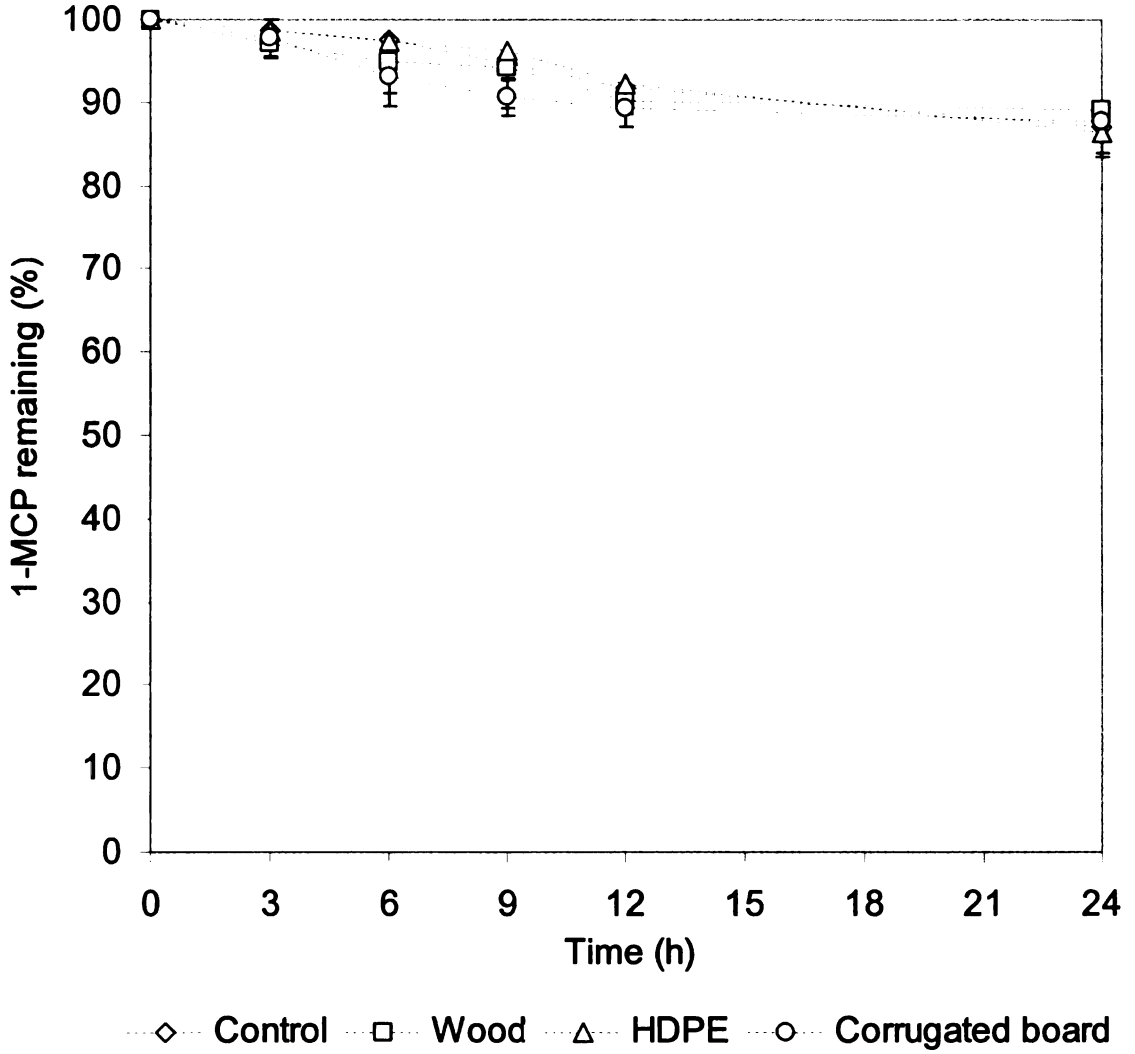


Figure 3.1 Effects of wood (*Gmelina arboreus*), HDPE and corrugated board on 1-MCP concentration at 20°C and 50% RH. Control was a 1-L empty jar.

Figure 3.2 shows the results for the concentrations in the glass jars at conditions of 20°C and 80% RH. Each value is the average of three determinations. Vertical lines represent standard deviation.

Under these conditions, the difference between corrugated board and the other materials tested became more evident. After 24 hours, the concentration of 1-MCP had declined slightly for wood and HDPE, and for the control treatment. For these treatments, the average percentage loss was between 10-12%.

As for the corrugated board, the loss of 1-MCP was estimated to be 10% within the first 6 h, 27% after 9 h, 33% after 12 hours and 43% at the end of the 24 h exposure period. The apparent reduction of 1-MCP in the presence of corrugated board occurred within the first 12 hours, and any additional loss occurred at a much lower rate during the following 12 hours of the exposure period.

As expected, change in relative humidity had a significant effect on the moisture content of corrugated board and melina wood. The moisture content of corrugated board after 24 h treatment with 1-MCP was 8% when held at 50% RH, and 11% when held at 80%. For wood, the moisture content was 12% when held at 50% RH, and 19% when held at 80% RH.

These differences in the moisture content of wood and corrugated board suggest that the reduction of initial 1-MCP in the headspace of the jars might be a relative humidity dependent process that is more evident with corrugated board than it is with wood and HDPE.

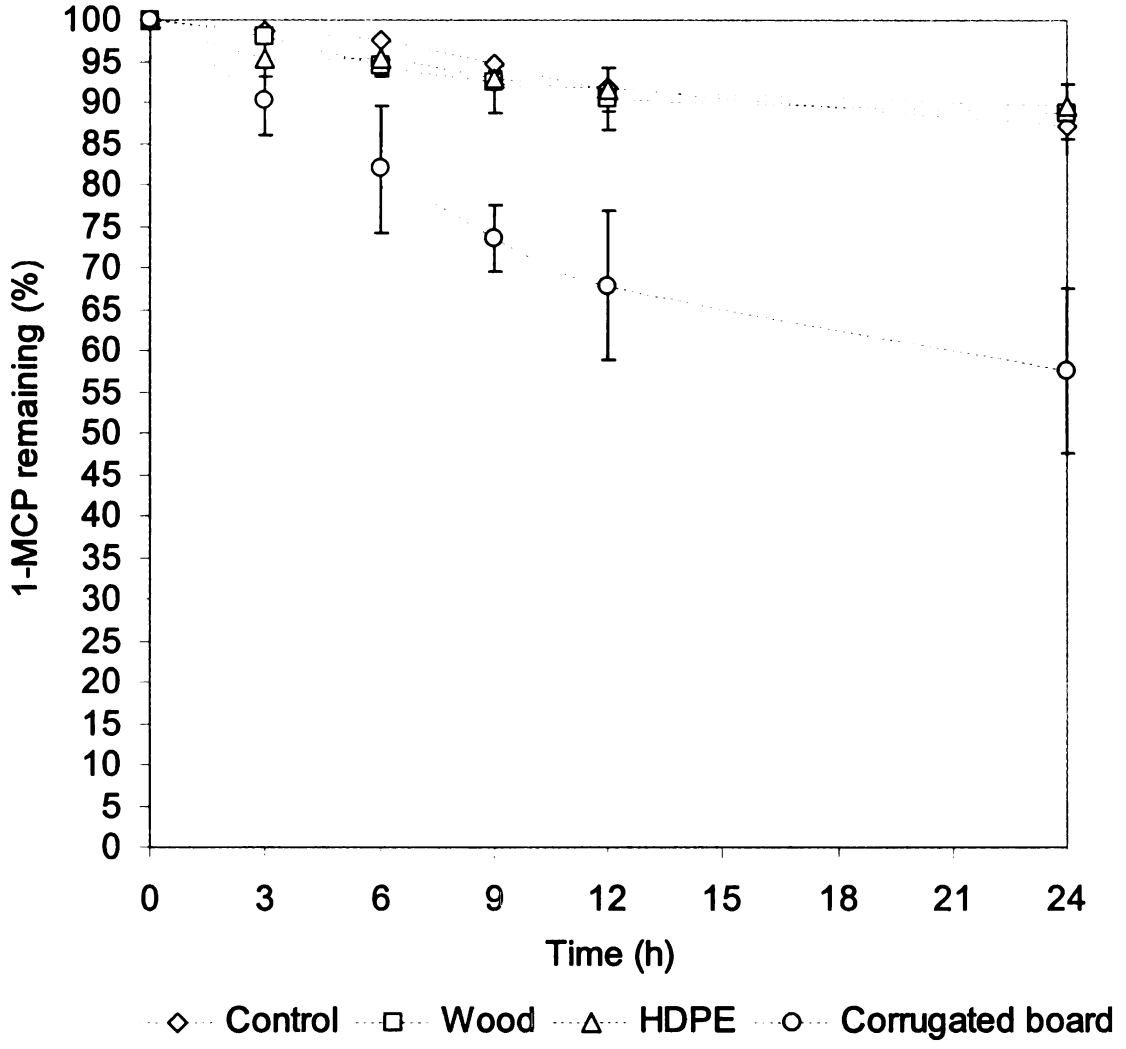


Figure 3.2 Effects of wood (*Gmelina arboreus*), HDPE and corrugated board on 1-MCP concentration at 20°C, 80% RH. Control was a 1-L empty jar.

*3.3.2 Evaluation of the effect of relative humidity, amount of packaging material in the treatment chamber, and initial concentration on availability of 1-MCP.*

The concentration of 1-MCP in the headspace of the treatment chamber in the presence of corrugated fiberboard and HDPE boxes at 20°C and 50%, 80% and 95% RH is shown in Figures 3.3 through 3.5. Each value is the average of three determinations. Vertical bars represent standard deviation.

In general, it was observed that the effective concentration of 1-MCP was markedly reduced in the presence of corrugated board, the percentage loss of 1-MCP over time was greater at higher relative humidities and slightly lower with increasing initial gas concentrations.

Different relative humidities had a significant effect on the moisture content of corrugated board. The moisture content of corrugated board at the end of treatment with 1-MCP was 2.7%, 10.3% and 11.0% when held at 50%, 80%, and 95% RH, respectively. These differences in moisture content suggest that the reduction of initial 1-MCP in the headspace of the jars is a relative humidity-dependent process.

Consistent with previous results, there was little interaction between HDPE and 1-MCP over time. Nonetheless, the relative loss of 1-MCP over time in the presence of HDPE based materials also increased slightly at higher relative humidities, the effect of amount of material present or the initial concentration in the chamber headspace was less evident though. Experimental error associated with sampling method or injection technique of the sample in the GC may have caused some differences.

A preliminary evaluation of the treatment chambers showed that the system experienced a loss of 3% over a treatment period of 24 h when the initial concentration of 1-MCP was 5 μL $L^{-1}$ of 1-MCP.

These results suggest that the loss of 1-MCP in the presence of corrugated HDPE boxes might be explained by interactions of the gas molecule with the moisture in the airspace and the HDPE material; or might also be an indication of some molecular instability.

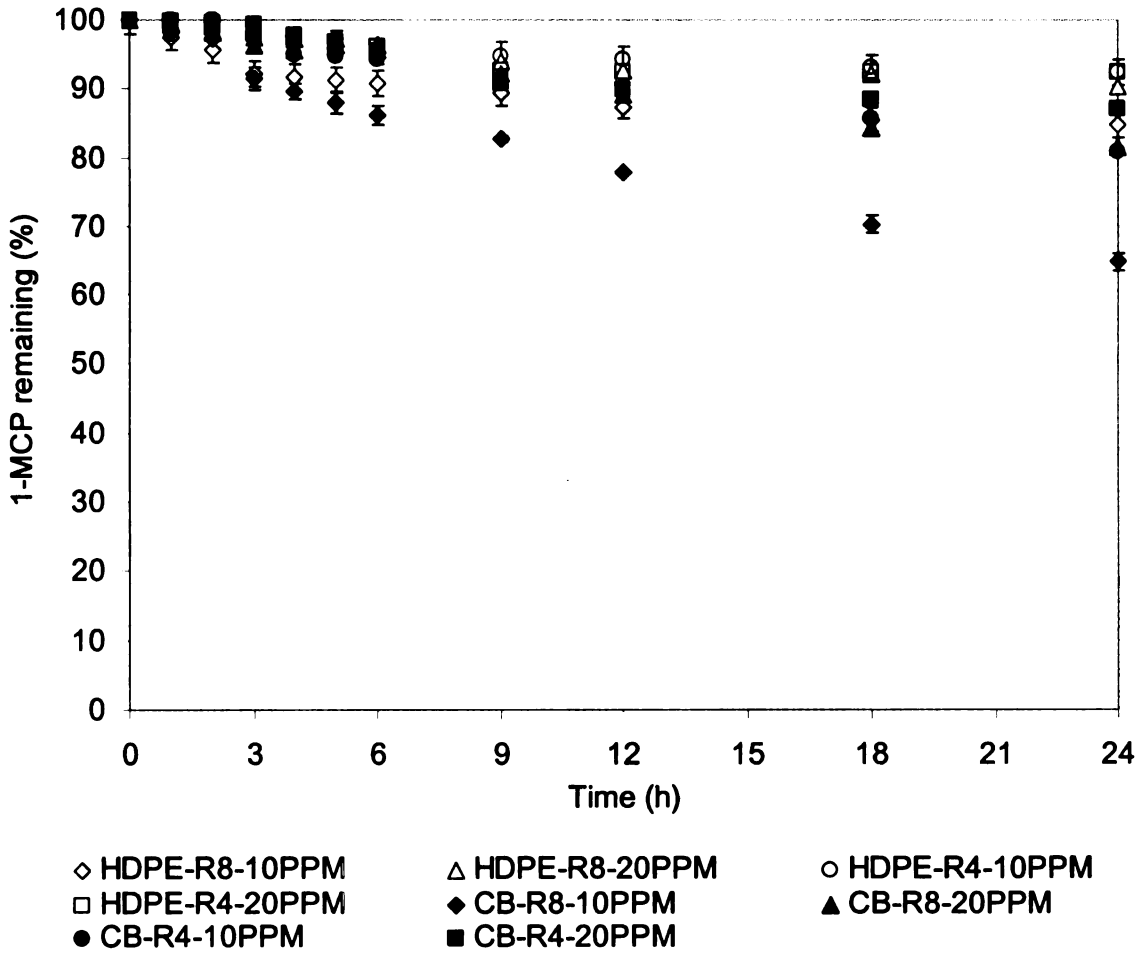


Figure 3.3 Effect of amount of HDPE and corrugated board and initial concentration of 1-MCP on percentage (%) available 1-MCP at 20°C, 50% RH.

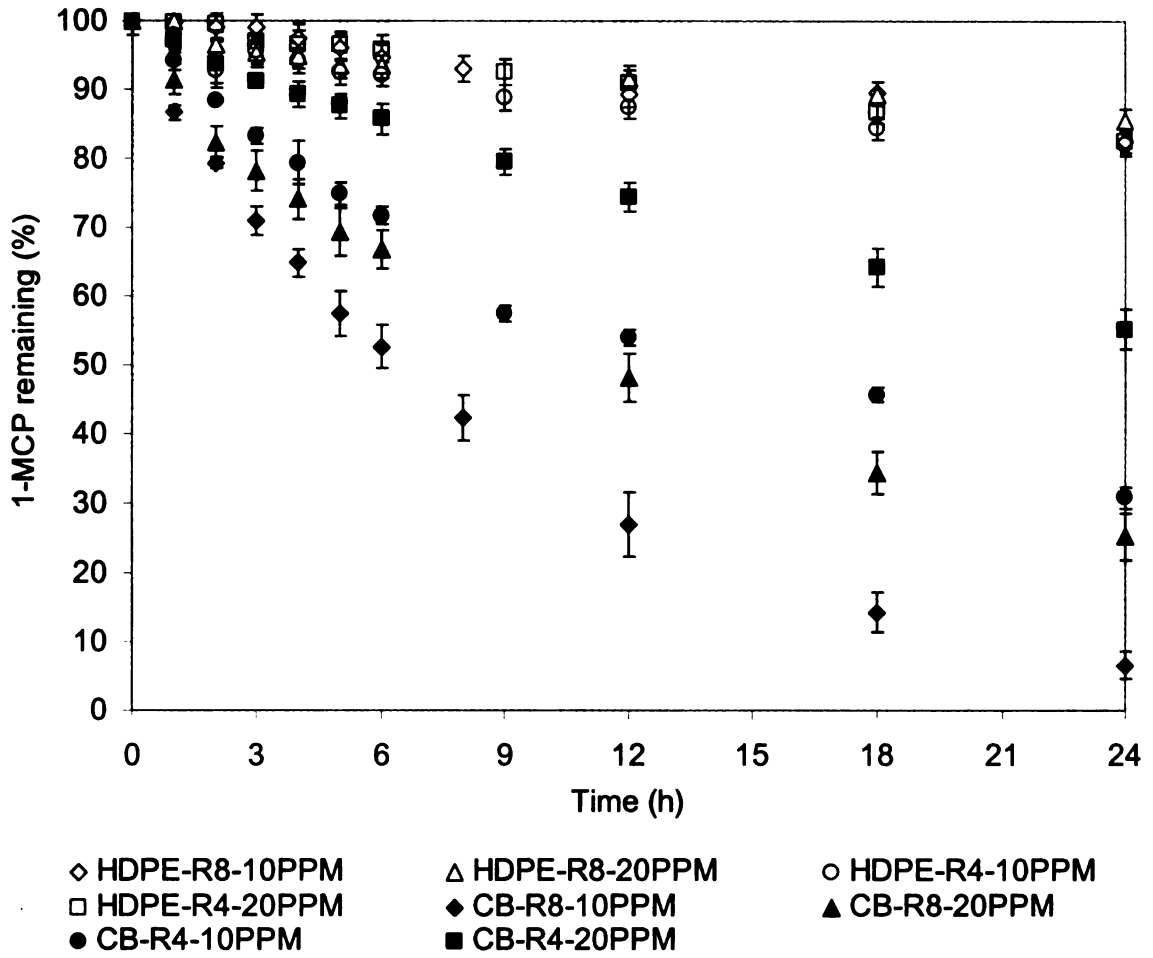


Figure 3.4 Effect of amount of HDPE and corrugated board and initial concentration of 1-MCP on percentage (%) available 1-MCP at 20°C, 80% RH.

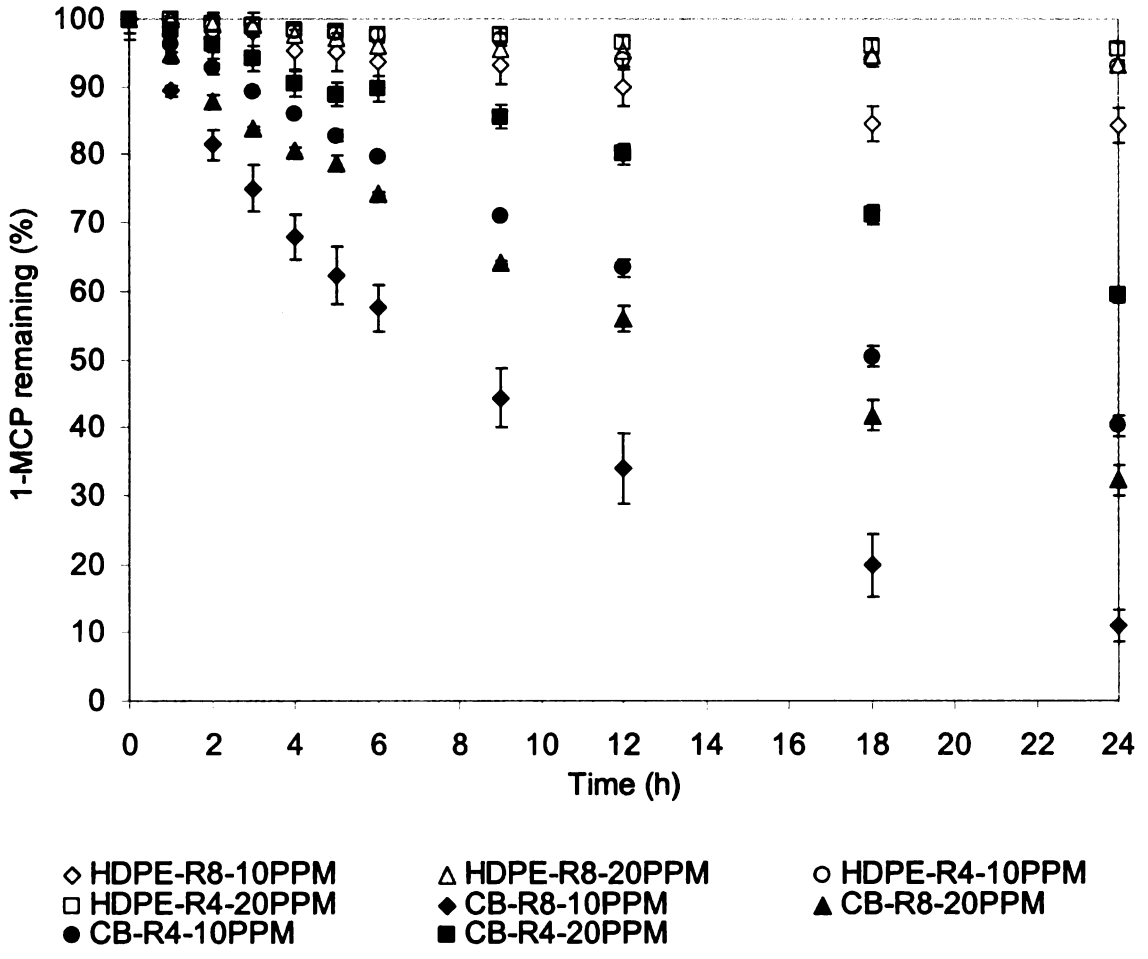


Figure 3.5 Effect of amount of HDPE and corrugated board and initial concentration of 1-MCP on percentage (%) available 1-MCP at 20°C, 95% RH.

Results from Figures 3.3 – 3.5 suggest that:

- The reduction in mass of 1-MCP over time is proportional to mass of 1-MCP (initial concentration in treatment chamber) and to treatment time.
- Concentration of 1-MCP at any time *t* seems to follow a declining behavior that can be fitted by an exponential model (1):

$$C_t = C_0 e^{-kt} \qquad (1)$$

where $C_t$ is the concentration of 1-MCP at any time *t*, $C_0$ is the initial concentration of 1-MCP, *e* is the base of the natural logarithm, and *k* is a constant related to the rate at which 1-MCP gas is removed from the chamber headspace with units given by 1/*t*.

To remove subjectivity associated with the visual inspection of the plotted data, some criterion was devised to establish a basis for the fit. Nonlinear regression techniques are available to directly fit equations to experimental data directly (Chapra and Canale, 1998). However, a simpler alternative was to use mathematical calculation to transform expression (1) into a linear form.

Expression (1) was linearized by taking its natural logarithm to yield:

$$\ln C_t = \ln C_0 - kt \qquad (2)$$

In its transformed state, linear regression was used to fit the model in order to evaluate the constant coefficient *k* using the technique of least squares regression. For a given ratio of mass of packaging material (kg) per unit volume ($m^3$) of airspace in the treatment chamber, relative humidity, and initial concentration of 1-MCP; the best fit *k* values were the ones that minimized the

sum of squares of the errors (SSE) between the experimental concentration of 1-MCP in the treatment chamber and the predicted concentrations using (2).

The best-fit *k* values are given by (3):

$$SSE = \sum_{i=1}^{\infty} [\ln C_i - (\ln C_0 - kt_i)]^2 \qquad (3)$$

It can be shown that the partial differential equation of expression (3) with respect to *k* can be solved to find the best-fit values using the following expression (4):

$$\frac{\partial SSE}{\partial k} = 0 = 2 \sum_{i=1}^{\infty} [t_i \ln (C_i / C_0 + kt_i^2] \qquad (4)$$

Solving (4) gives (5):

$$k = - \frac{\Sigma\ t_i \ln (C_i / C_0)}{\Sigma\ t_i^2} \qquad (5)$$

Expression (5) gives the experimental k values for a given ratio of mass of packaging material (kg) per unit volume ($m^3$) of airspace in the treatment chamber, relative humidity, and initial concentration of 1-MCP. Tables 3.2 & 3.3 provide a summary of the results and also show the sum of squares of the errors (SSE) between the experimental and predicted concentrations of 1-MCP in the treatment chamber.

Table 3.2 Values of *k* for the exponential model $C_t = C_0e^{-kt}$ fit to the concentration of 1-MCP in the chambers containing *HDPE* boxes at different relative humidities (RH), initial concentrations of gas 1-MCP (10 and 20 μL $L^{-1}$) and ratios of packaging material (R = $kg/m^3$).

| RH | R ($kg/m^3$) | 1-MCP (μL $L^{-1}$) | k (1/h) | SSE (μL $L^{-1}$) |
|---|---|---|---|---|
| 50 | 4 | 10 | 0.004122 | 0.0020 |
| | 4 | 20 | 0.004609 | 0.0031 |
| | 8 | 10 | 0.009192 | 0.0147 |
| | 8 | 20 | 0.004935 | 0.0013 |
| 80 | 4 | 10 | 0.008254 | 0.0104 |
| | 4 | 20 | 0.007393 | 0.0007 |
| | 8 | 10 | 0.007317 | 0.0018 |
| | 8 | 20 | 0.006318 | 0.0044 |
| 95 | 4 | 10 | 0.003537 | 0.0007 |
| | 4 | 20 | 0.002343 | 0.0004 |
| | 8 | 10 | 0.008218 | 0.0017 |
| | 8 | 20 | 0.003460 | 0.0011 |

Table 3.3 Values of *k* for the exponential model $C_t = C_0e^{-kt}$ fit to the concentration of 1-MCP in the chambers containing *corrugated fiberboard* boxes at different relative humidities (RH), initial concentrations of 1-MCP (10 and 20 μL $L^{-1}$) and ratios of packaging material (R = $kg/m^3$)

| RH | R ($kg/m^3$) | 1-MCP (μL $L^{-1}$) | k (1/h) | SSE (μL $L^{-1}$) |
|---|---|---|---|---|
| 50 | 4 | 10 | 0.008933 | 0.0007 |
| | 4 | 20 | 0.006833 | 0.0031 |
| | 8 | 10 | 0.019517 | 0.0058 |
| | 8 | 20 | 0.008893 | 0.0006 |
| 80 | 4 | 10 | 0.050360 | 0.0317 |
| | 4 | 20 | 0.024026 | 0.0018 |
| | 8 | 10 | 0.104053 | 0.0620 |
| | 8 | 20 | 0.062310 | 0.0341 |
| 95 | 4 | 10 | 0.038026 | 0.0000 |
| | 4 | 20 | 0.020230 | 0.0038 |
| | 8 | 10 | 0.093404 | 0.0076 |
| | 8 | 20 | 0.048169 | 0.0036 |

These experimental *k* values were substituted in expression (1) and the adequacy of the mathematical model for each given ratio of packaging material (Kg per cubic meter of airspace), relative humidity, and initial concentration, was tested by plotting the calculated 1-MCP concentration along with the experimental data collected versus time. Figures 3.6 to 3.17 illustrate the results obtained. Each value is the average of three determinations. Vertical lines represent standard deviation.

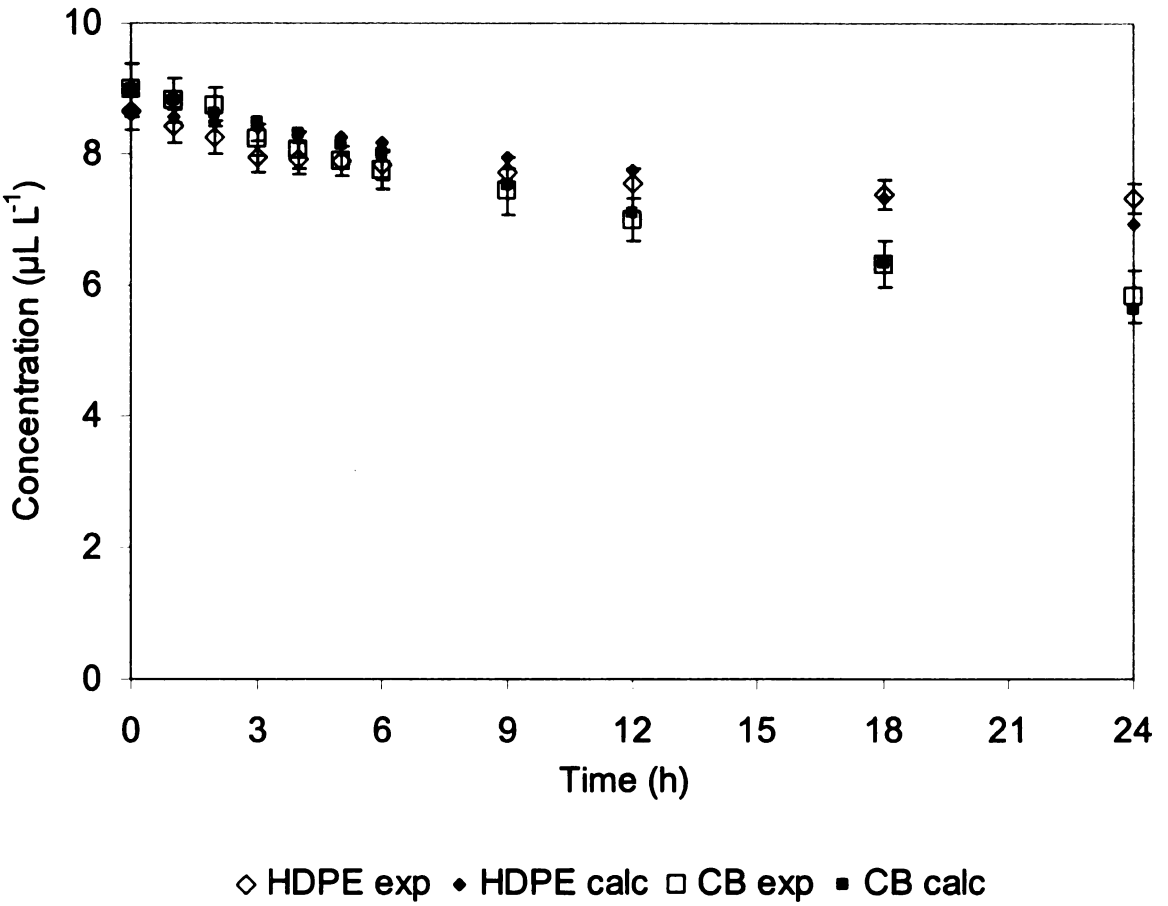


Figure 3.6 Comparison of experimental and calculated concentration values of 1-MCP in a sealed treatment chamber with a material ratio of 8 kg/m$^3$ and an initial concentration of 10 µL L$^{-1}$ held at 20°C and 50% RH for 24 h.

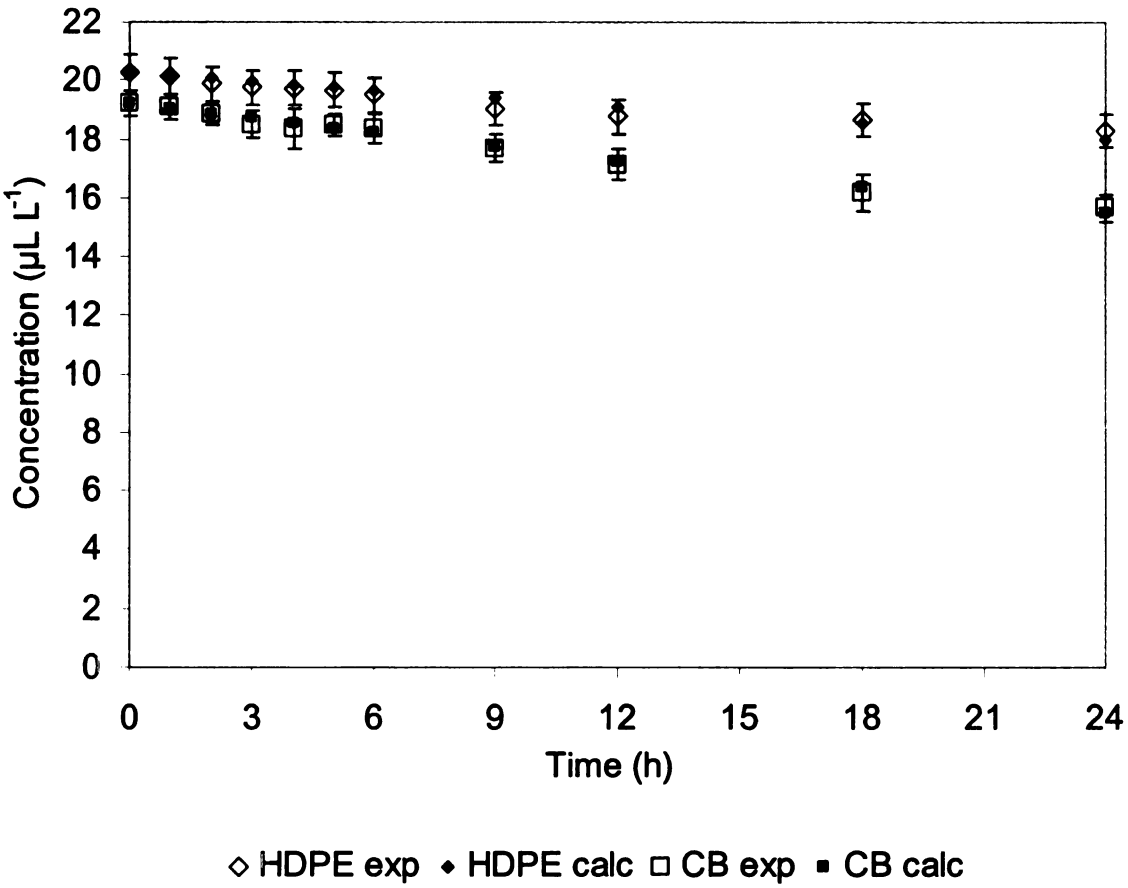


Figure 3.7 Comparison of experimental and calculated concentration values of 1-MCP in a sealed treatment chamber with a material ratio of 8 kg/m$^3$ and an initial concentration of 20 µL L$^{-1}$ held at 20°C and 50% RH for 24 h.

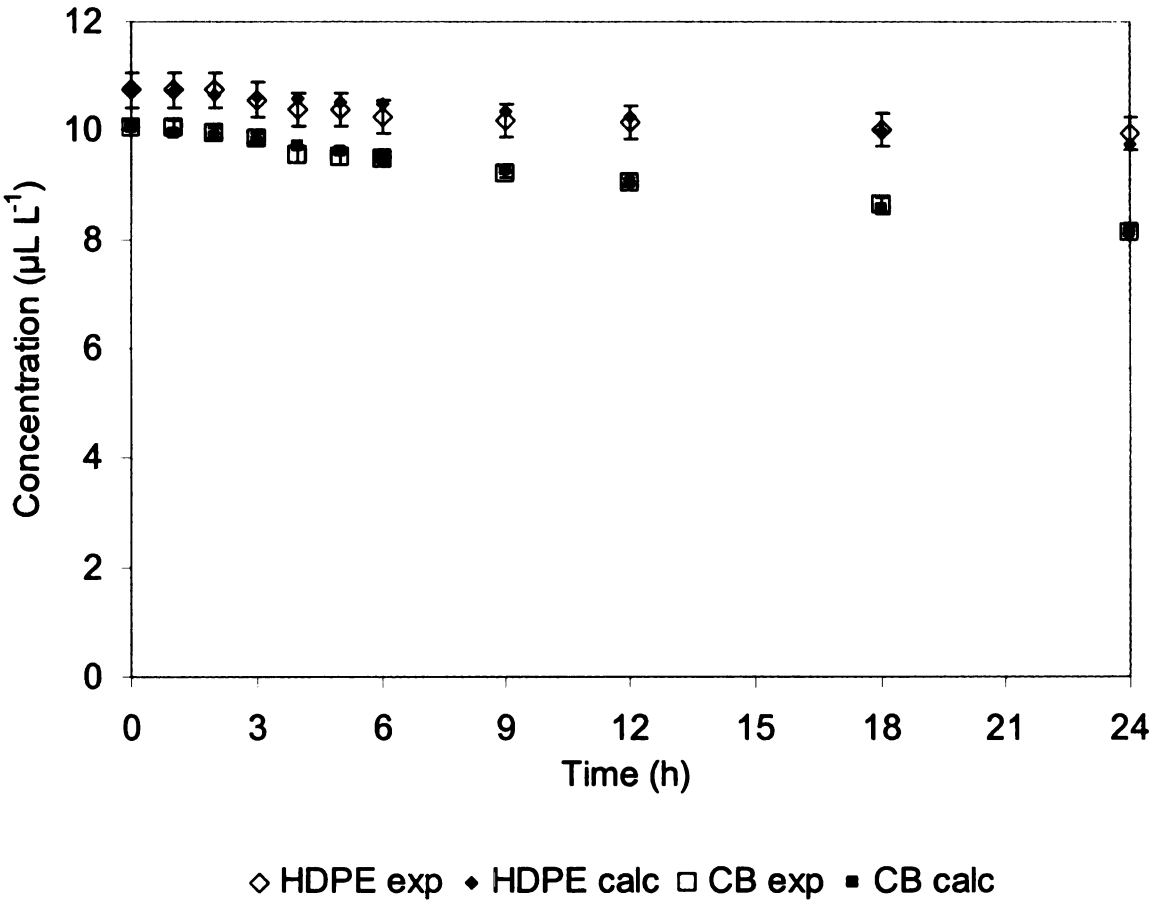


Figure 3.8 Comparison of experimental and calculated concentration values of 1-MCP in a sealed treatment chamber with a material ratio of 4 kg/m$^3$ and an initial concentration of 10 µL L$^{-1}$ held at 20°C and 50% RH for 24 h.

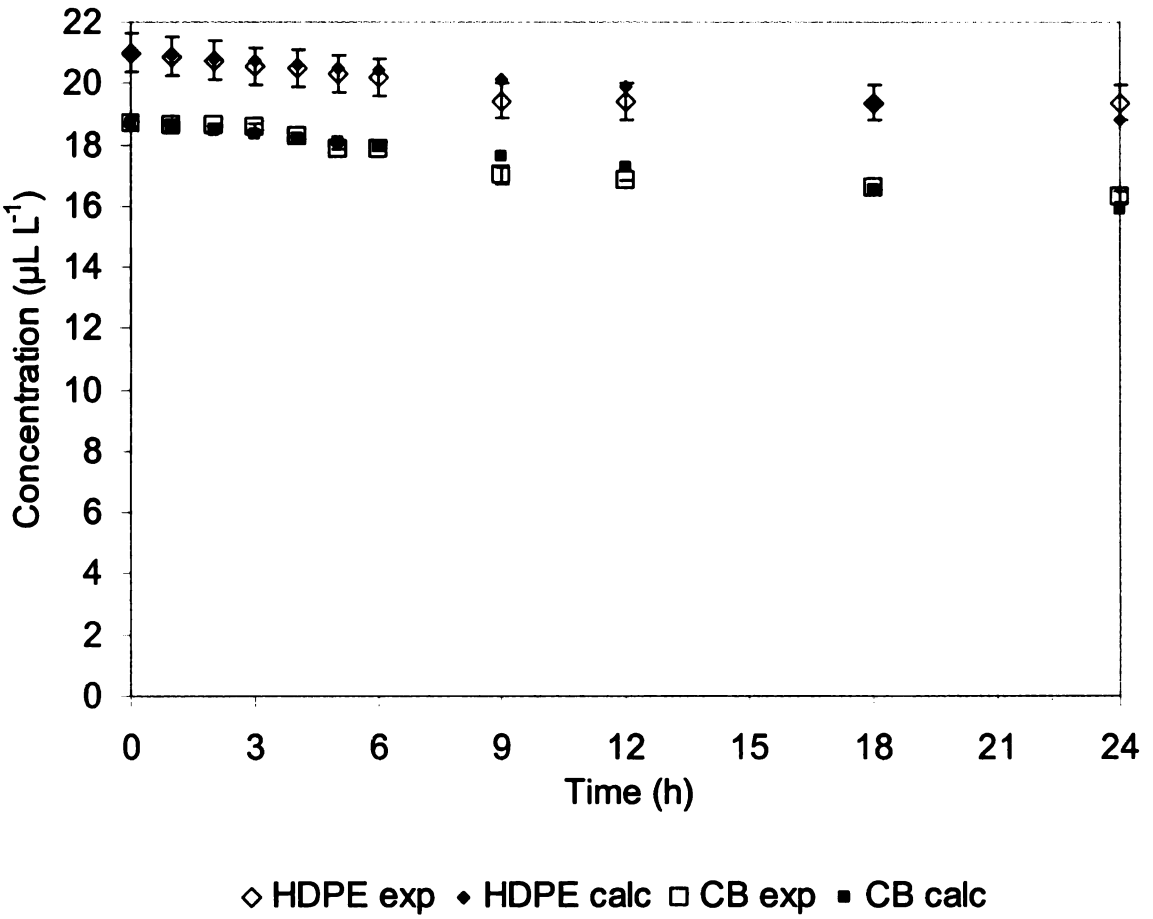


Figure 3.9 Comparison of experimental and calculated concentration values of 1-MCP in a sealed treatment chamber with a material ratio of 4 kg/m$^3$ and an initial concentration of 20 µL L$^{-1}$ held at 20°C and 50% RH for 24 h.

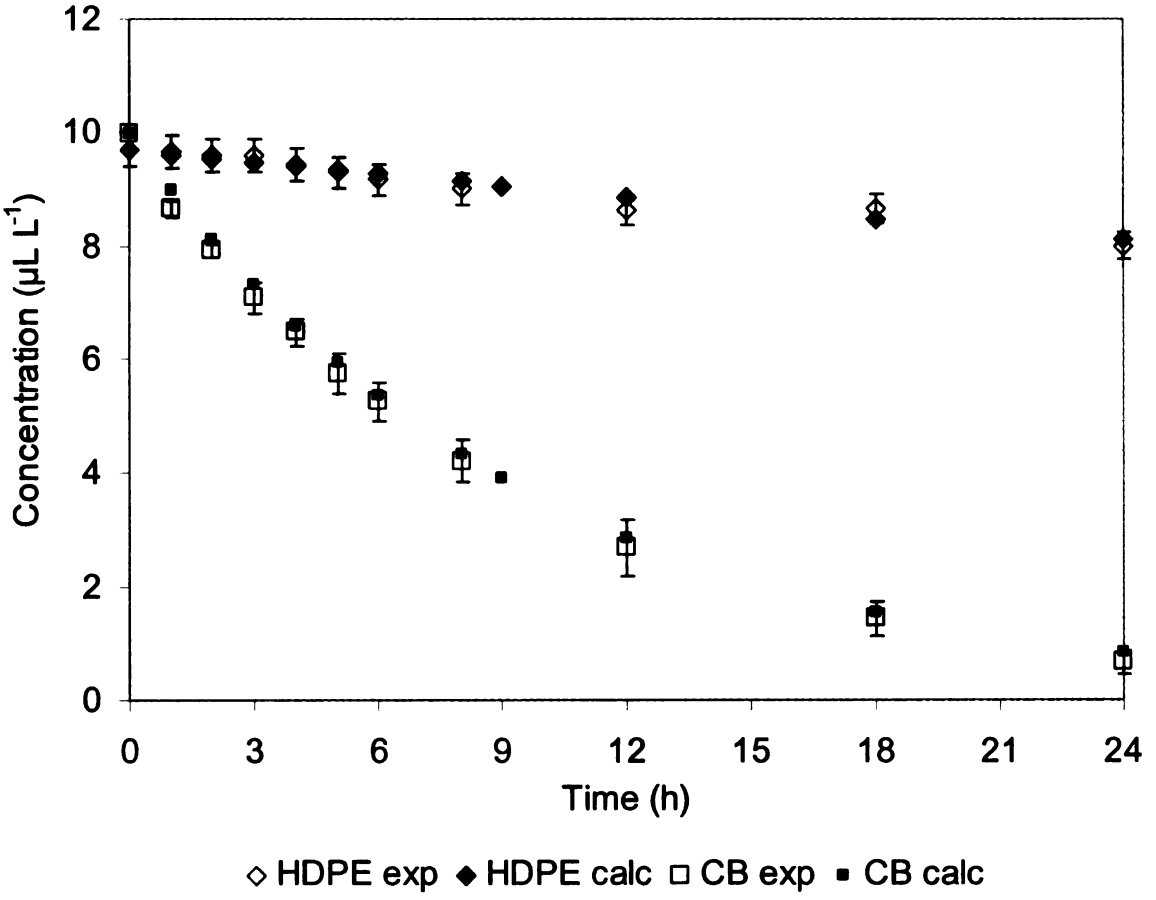


Figure 3.10 Comparison of experimental and calculated concentration values of 1-MCP in a sealed treatment chamber with a material ratio of 8 kg/m$^3$ and an initial concentration of 10 µL L$^{-1}$ held at 20°C and 80% RH for 24 h.

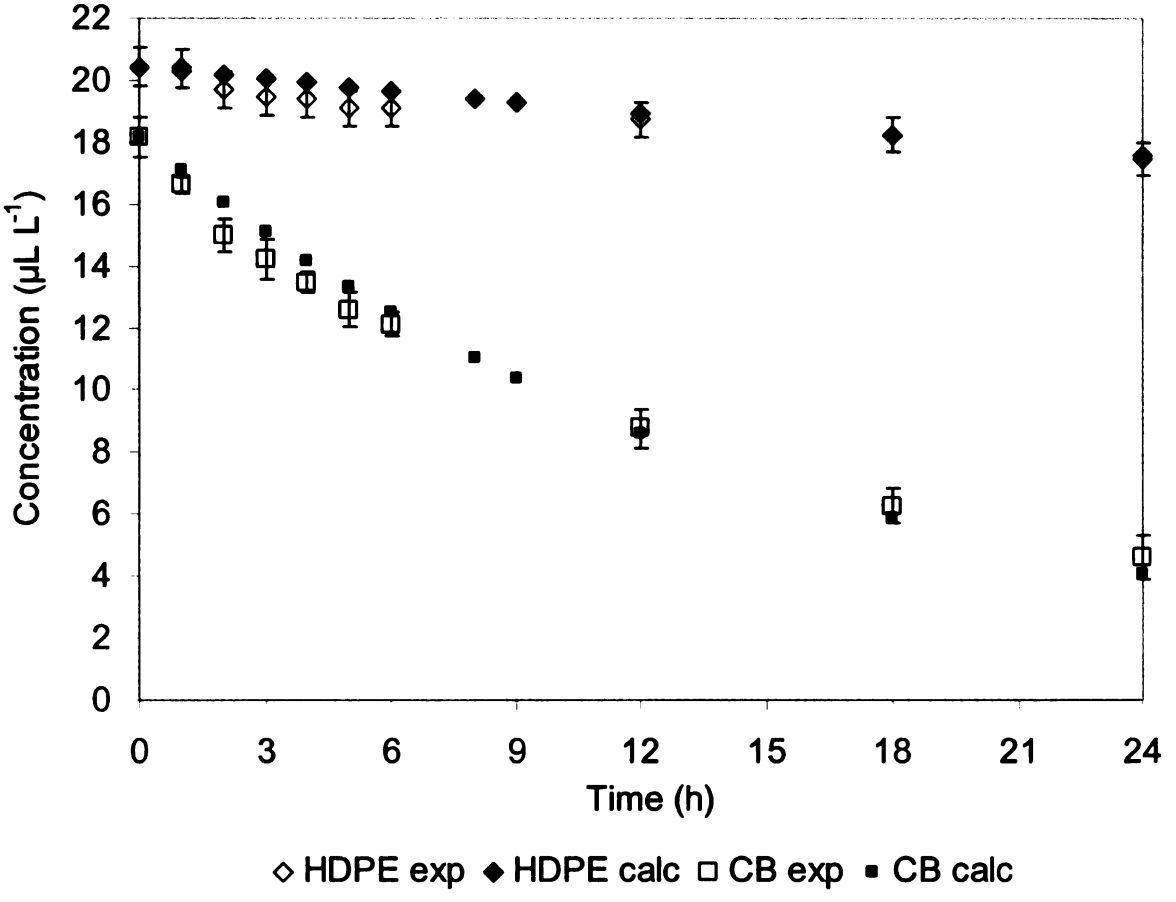


Figure 3.11 Comparison of experimental and calculated concentration values of 1-MCP in a sealed treatment chamber with a material ratio of 8 kg/m$^3$ and an initial concentration of 20 µL L$^{-1}$ held at 20°C and 80% RH for 24 h.

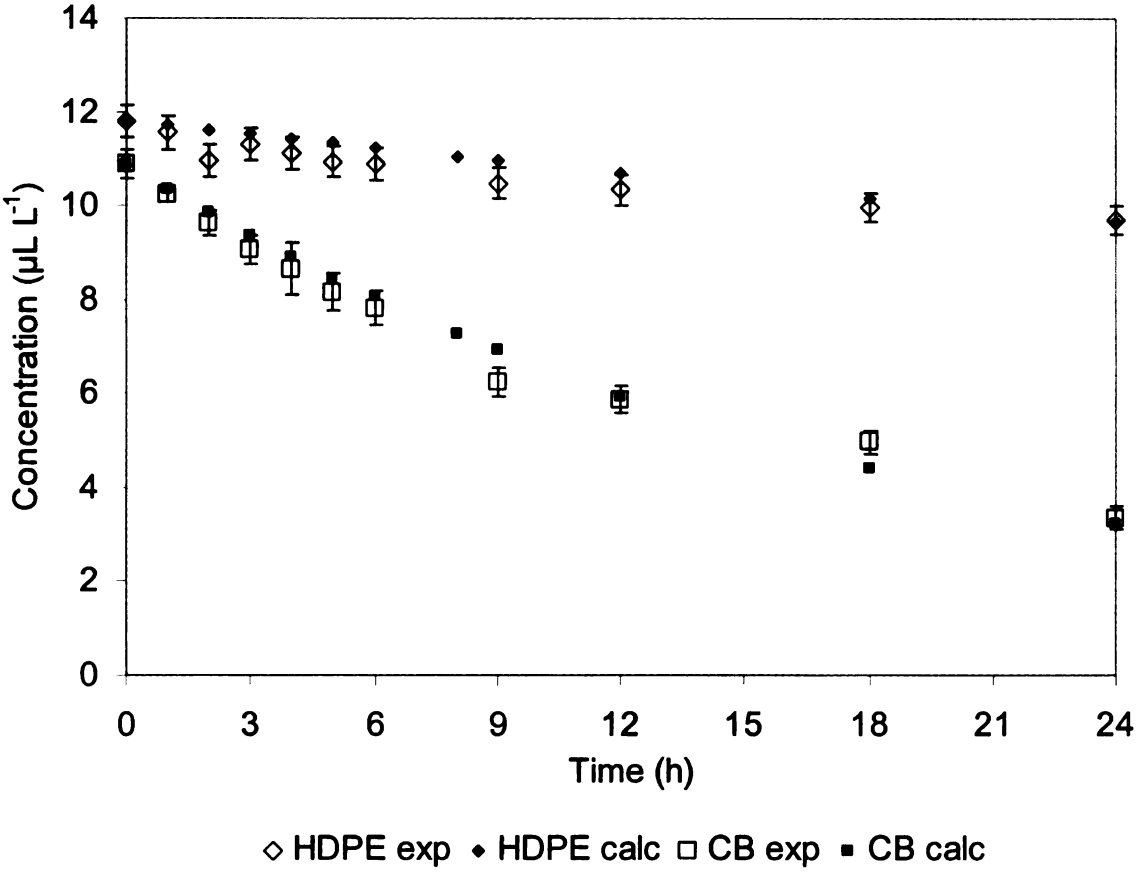


Figure 3.12 Comparison of experimental and calculated concentration values of 1-MCP in a sealed chamber treatment chamber with a material ratio of 4 kg/m$^3$ and an initial concentration of 10 µL L$^{-1}$ held at 20°C and 80% RH for 24 h.

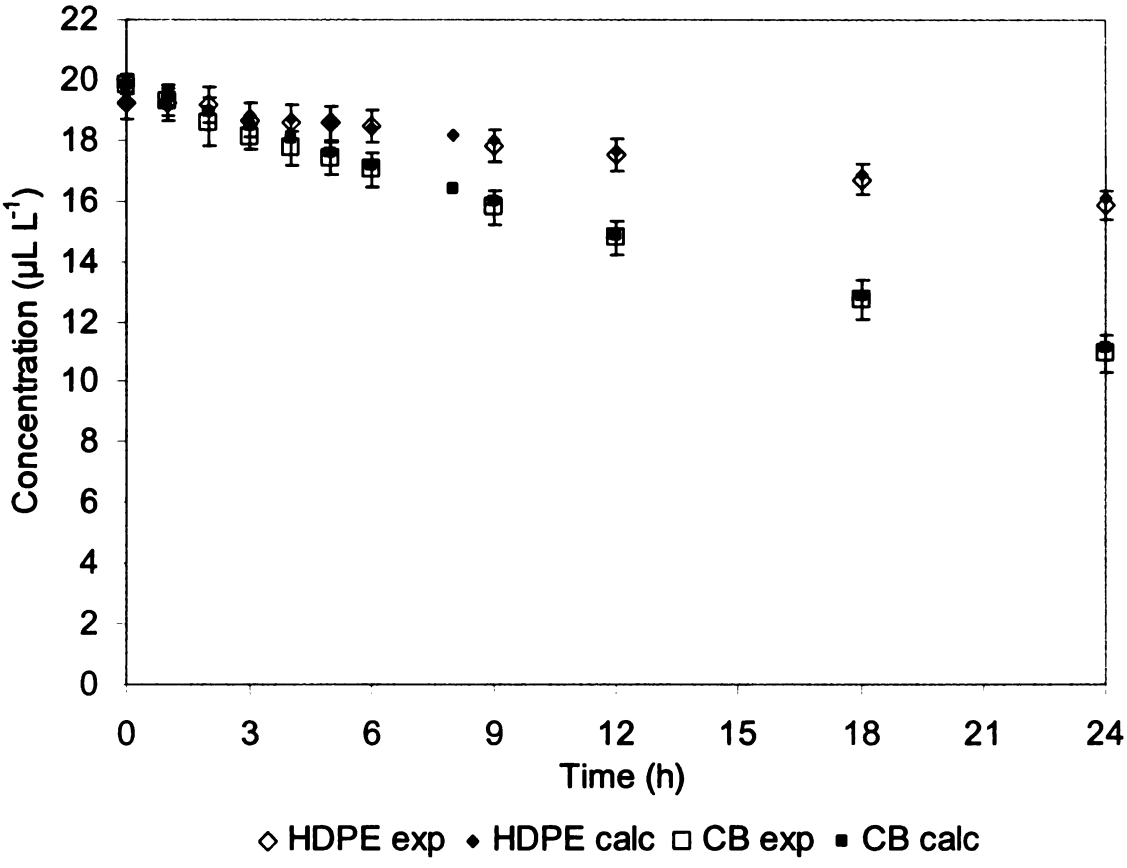


Figure 3.13 Comparison of experimental and calculated concentration values of 1-MCP in a sealed treatment chamber with a material ratio of 4 kg/m$^3$ and an initial concentration of 20 µL L$^{-1}$ held at 20°C and 80% RH for 24 h.

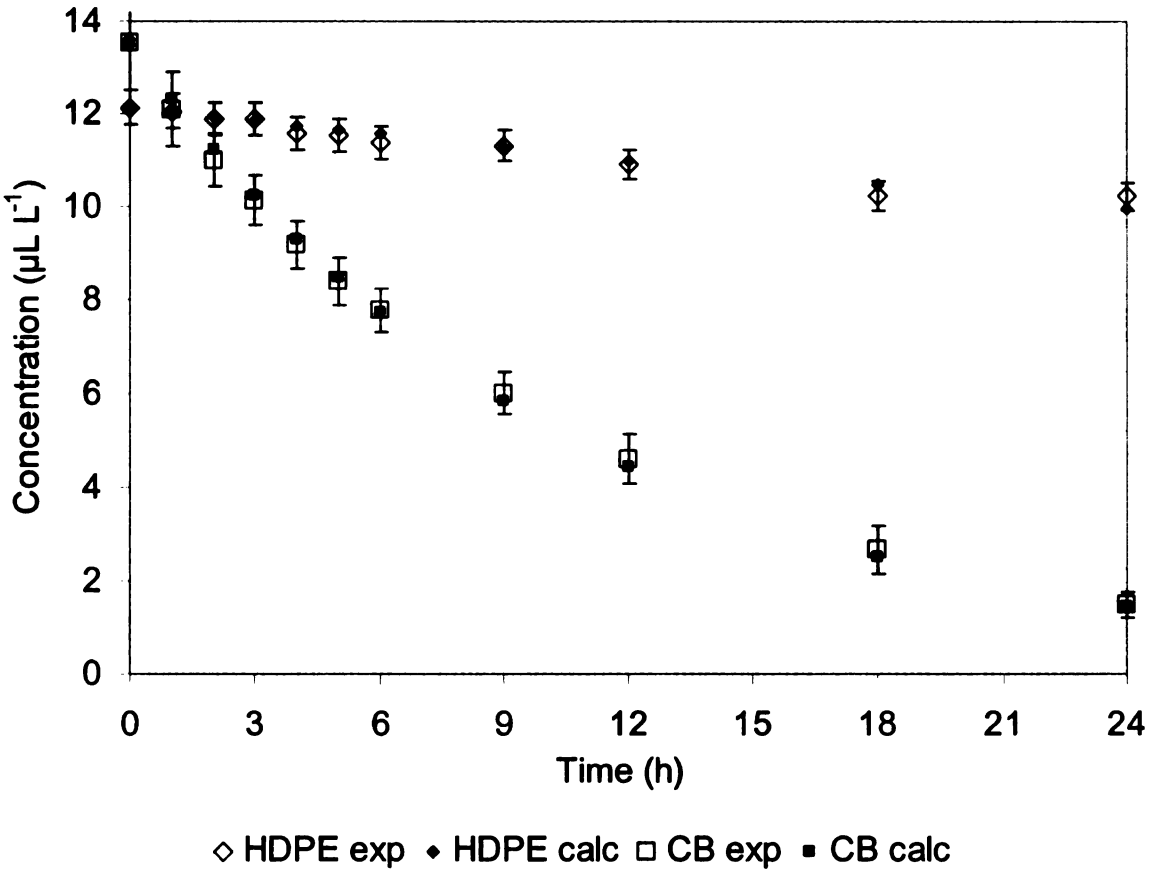


Figure 3.14 Comparison of experimental and calculated concentration values of 1-MCP in a sealed treatment chamber with a material ratio of 8 kg/m$^3$ and an initial concentration of 10 µL L$^{-1}$ held at 20°C and 95% RH for 24 h.

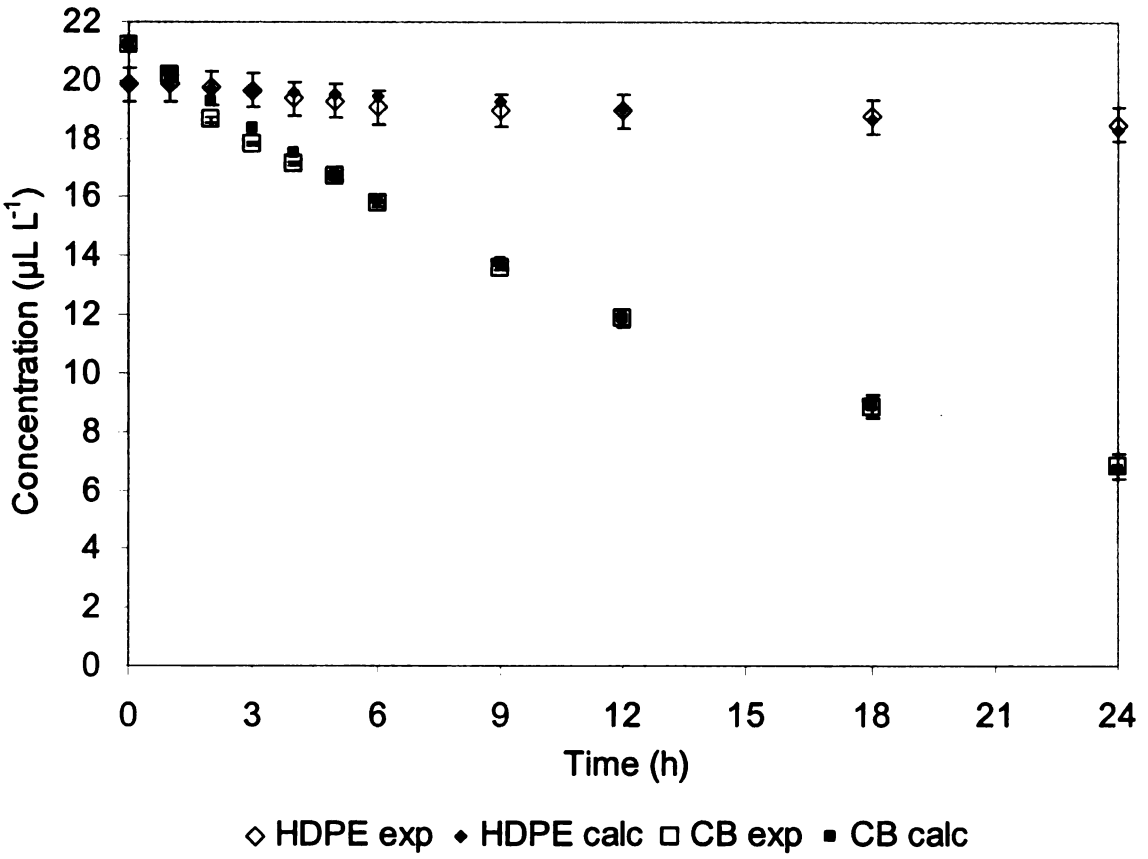


Figure 3.15 Comparison of experimental and calculated concentration values of 1-MCP in a sealed treatment chamber with a material ratio of 8 kg/m$^3$ and an initial concentration of 20 µL L$^{-1}$ held at 20°C and 95% RH for 24 h.

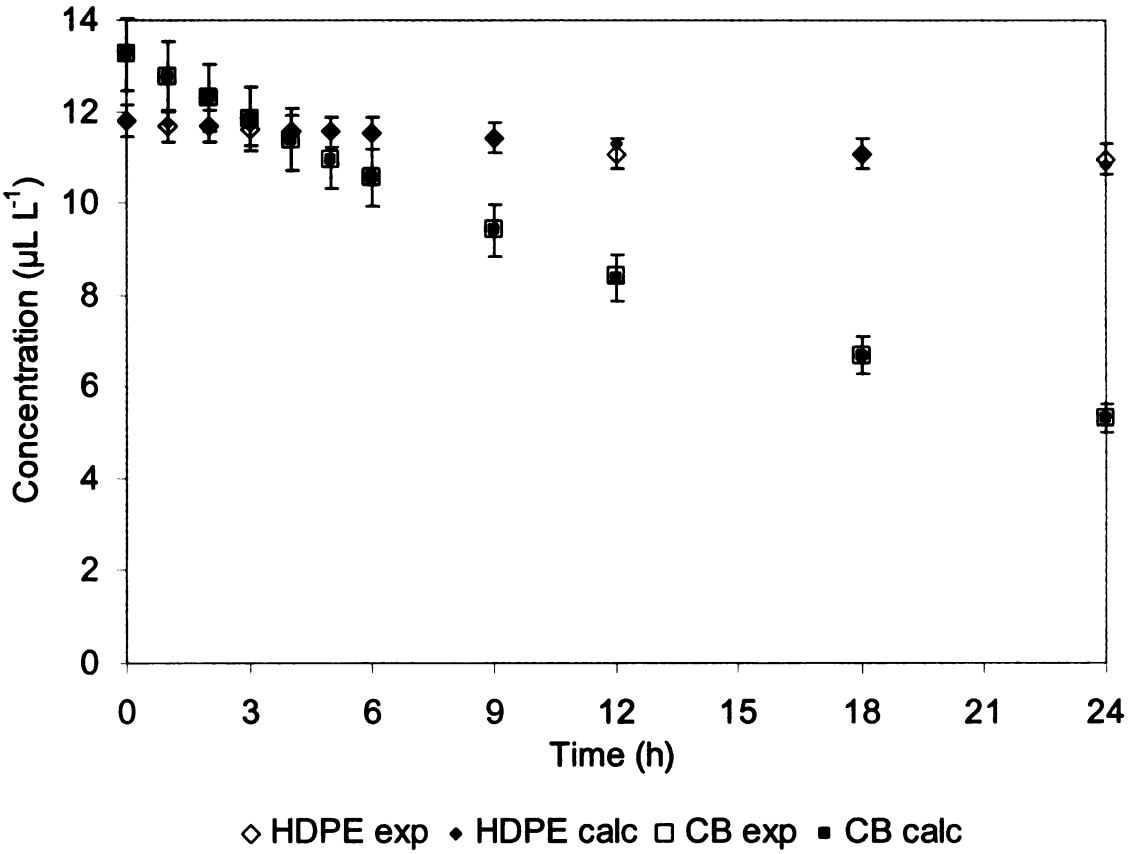


Figure 3.16 Comparison of experimental and calculated concentration values of 1-MCP in a sealed treatment chamber with a material ratio of 4 kg/m$^3$ and an initial concentration of 10 µL L$^{-1}$ held at 20°C and 95% RH for 24 h.

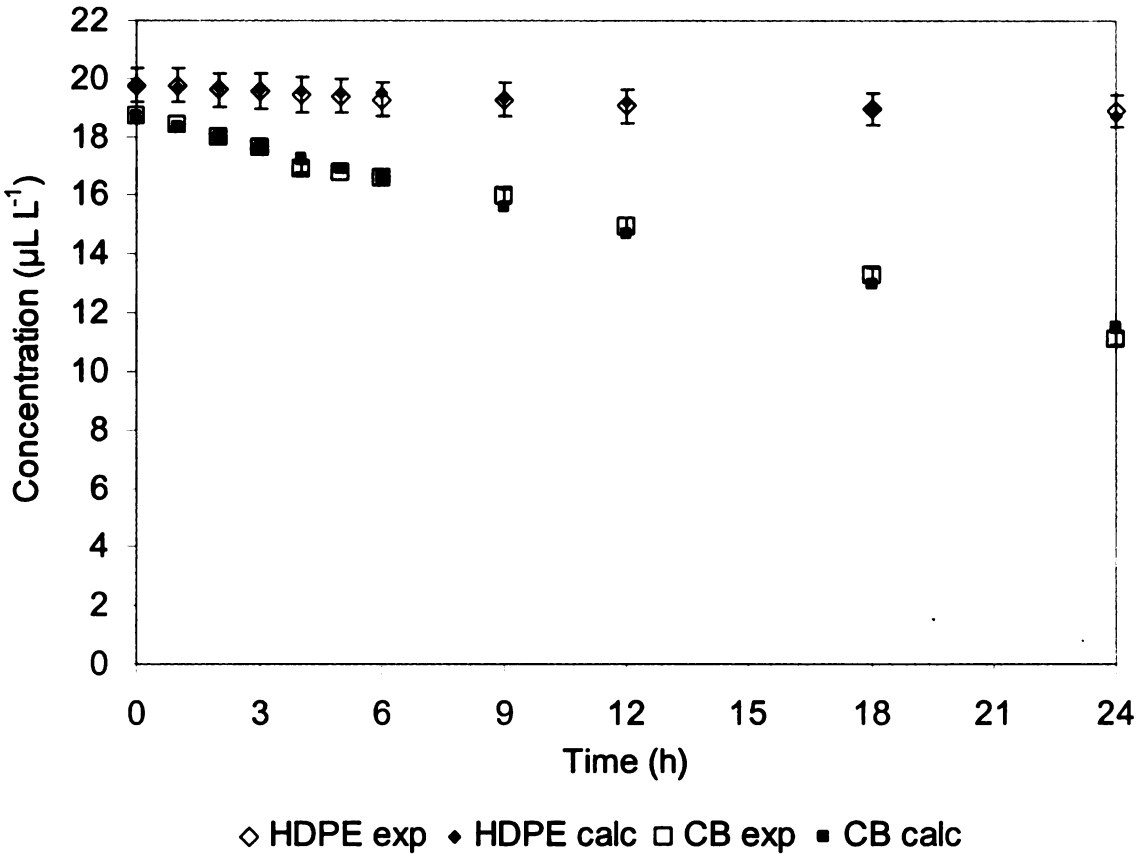


Figure 3.17 Comparison of experimental and calculated concentration values of 1-MCP in a sealed treatment chamber with a material ratio of 4 kg/m$^3$ and an initial concentration of 20 µL L$^{-1}$ held at 20°C and 95% RH for 24 h.

These results, as plotted in figures 3.6 to 3.17, indicate that the exponential model $C_t = C_0e^{-kt}$ provides an excellent fit to the 1-MCP concentrations in the chamber headspaces containing the different packaging materials.

A detailed analysis of the effects of relative humidity, initial concentration of 1-MCP and amount of corrugated board in the airspace of the treatment chamber on the experimental *k* values follows.

The effect of relative humidity on experimental *k* values is shown in Table 3.3 and illustrated in figure 3.18. It can be observed that as the relative humidity increased from 50% to 80% the experimental *k* values differed markedly, up to 10-fold, though a slight decrease was observed at a relative humidity of 95%.

These observations suggest that the relationship between relative humidity (RH) and the experimental *k* values is curvilinear ($k \sim aRH^2 + bRH + c$).

The effect of mass of corrugated board relative to air volume (R) on experimental *k* values is illustrated in figure 3.19. These results suggest that the *k* values are directly proportional to the mass of corrugated board ($k \sim R$). In general, the *k* values doubled as the ratio of corrugated board increased from 4 to 8 kg/ $m^3$.

The effect of initial concentration of 1-MCP on experimental *k* values is illustrated in figure 3.20. As observed, an increased in the initial concentration of 1-MCP from 10 to 20 μL $L^{-1}$ reduced by half the *k* values, which suggested that the relationship between initial concentration ($C_0$) of 1-MCP and the experimental *k* values is inversely proportional ($k \sim 1/C_0$).

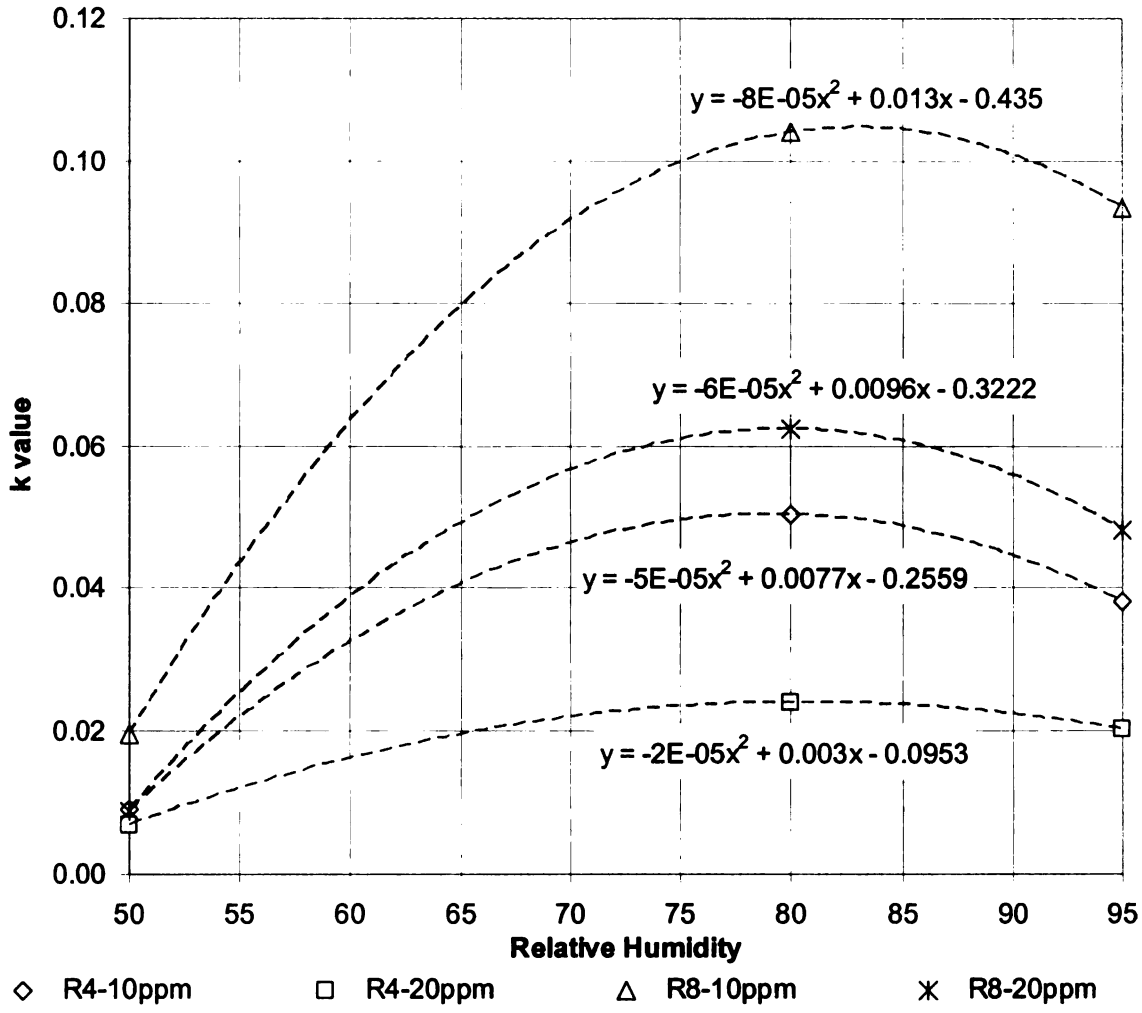


Figure 3.18 Effect of relative humidity on experimental k values in a sealed treatment chamber with a mass of corrugated board to air volume ratio (R) of 4 or 8 kg/m$^3$ and initial concentration of 1-MCP of 10 or 20 µL L$^{-1}$ applied at 20°C and 50%, 80%, and 95% RH for 24 h. The best fit equation is displayed next to its corresponding curve.

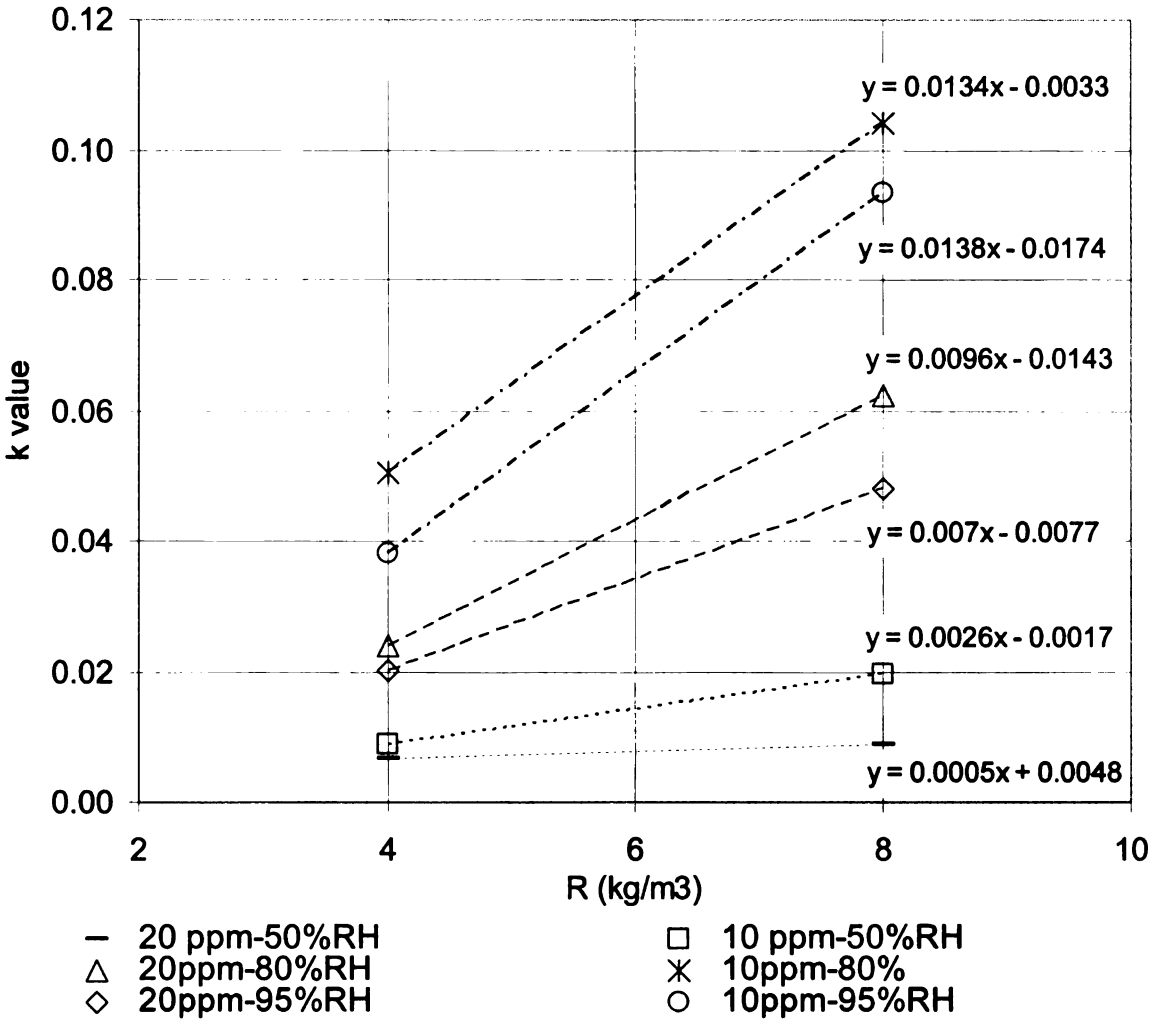


Figure 3.19 Effect of amount of mass of corrugated board to air volume ratio (R) on experimental k values at initial concentrations of 1-MCP of 10 or 20 μL $L^{-1}$ applied at 20°C and 50%, 80%, and 95% RH for 24 h; the mass of corrugated board relative to air volume ratio (R) varied from 4 to 8 kg/. The best fit equation is displayed next to its corresponding line.

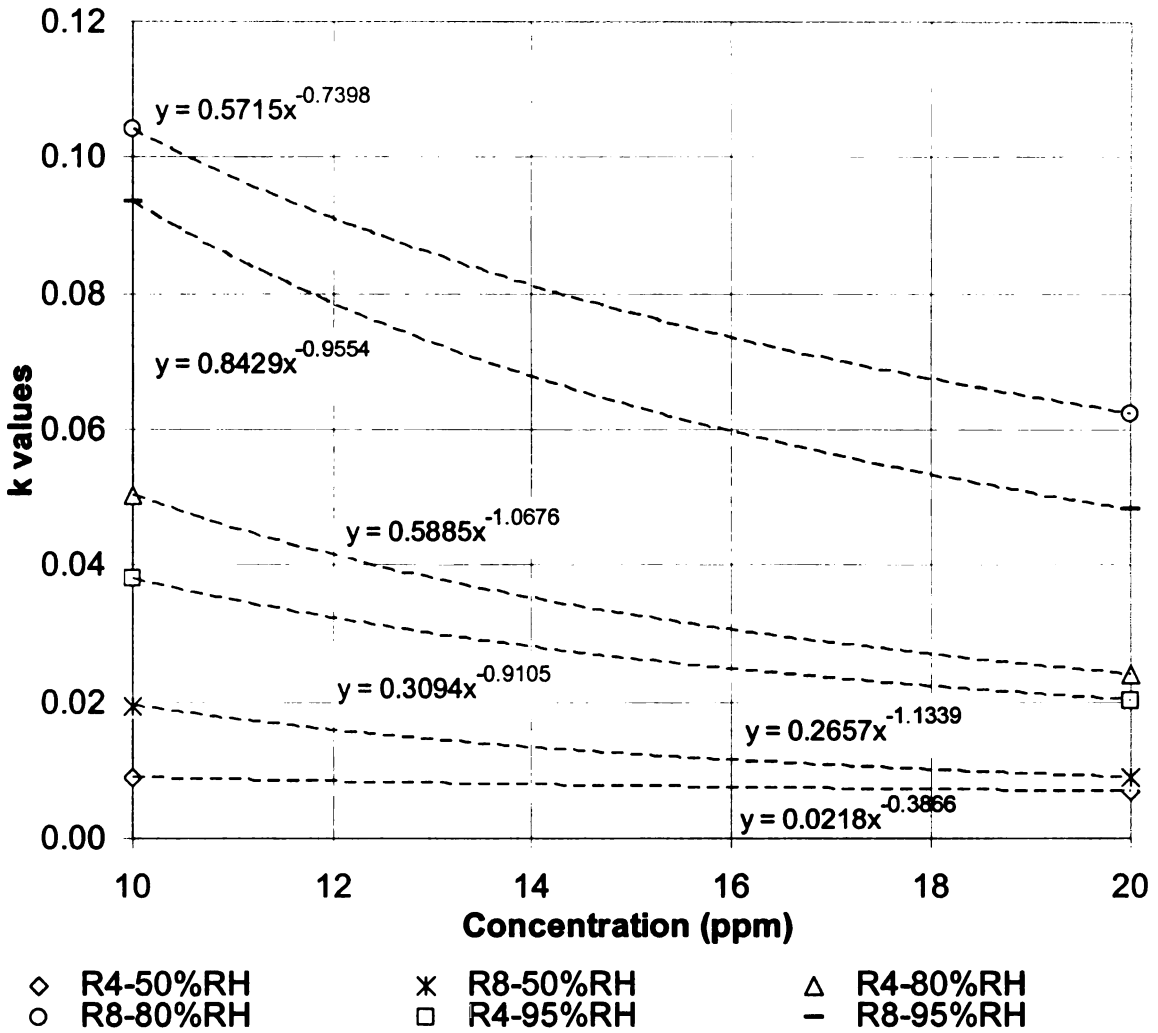


Figure 3.20 Effect of initial concentrations of 1-MCP on experimental k values when applied in a sealed treatment chamber with a mass of corrugated board to air volume ratio (R) of 4 or 8 kg/m$^3$ at 20°C and 50%, 80%, and 95% RH for 24 h. The best fit equation is displayed next to its corresponding line.

A similar analysis was conducted for HDPE boxes, it can be observed from Table 3.2 that (a) the effect of R on k is that k is proportional to R, as with CB, (b) except for R=8 and $C_0$=10, the effect of RH on k is curvilinear, as with CB, and (c) the effect of $C_0$ on k is an inverse one, just like with CB.

Results from the analysis presented above, suggest that the experimental values for the constant *k* related to the rate at which 1-MCP gas was removed from the headspace of the treatment chamber in the presence of both corrugated board or HDPE depended on the combined effect of relative humidity, initial concentration of 1-MCP and mass of material in the airspace of the treatment chamber.

This combined effect can be expressed by equation (6):

$$k = (R/C_0)(aRH^2 + bRH + c) \qquad (6)$$

where *k* is a constant related to the rate at which 1-MCP is removed from the headspace of the treatment chamber which units are 1/t (t is time in hours), R is the ratio of mass of corrugated board or HDPE (kg) per unit volume ($m^3$) of airspace in the treatment chamber, $C_0$ is the initial concentration, RH is the relative humidity, a, *b* and *c* are constants that relate relative humidity (RH) and the experimental *k* values.

A calculation was performed to estimate *k* for a given ratio of packaging material (kg) per cubic meter of airspace of the treatment chamber, relative humidity and initial concentration of 1-MCP, substituting (6) in (2) gives (7):

$$\ln C_i = \ln C_0 - [(R/C_0)(aRH^2 + bRH + c)t_i] \qquad (7)$$

Identifying the best *a*, *b* and *c* values was done using the technique of least squares regression. The best fit *a*, *b* and *c* values were the ones that minimized the sum of squares of the errors (SSE) between the experimental concentration of 1-MCP in the treatment chamber and the predicted concentrations using (8).

$$SSE = \sum_{i=1}^{\infty} [\ln C_i - (\ln C_0 - (R/C_0)(aRH^2 + bRH + c)t_i)]^2 = 0 \qquad (8)$$

Microsoft® GW-BASIC® was used to create a program to solve for *a*, *b* and *c* values. The best-fit values are shown in table 3.4, the sum of squares of the errors (SSE) between the experimental and predicted concentrations of 1-MCP in the treatment chamber is included.

Table 3.4 Best-fit for constants *a*, *b* and *c* and sum of squares of the errors (SSE) for high density polyethylene (HDPE) and corrugated board (CB) for the different relative humidities, initial concentrations of gas 1-MCP and ratios of packaging material tested.

| Material | a | b | c | SSE |
|---|---|---|---|---|
| HDPE | -0.0582 | 0.0829 | -0.0136 | 0.0000492 |
| CB | -1.1017 | 1.7955 | -0.5982 | 0.000183 |

Fitting expression (8) to the data gives the calculated *k* values. Tables 3.5 and 3.6 summarize the data obtained and also show the sum of squares of the errors (SSE) between the experimental and predicted concentrations (units are

μL $L^{-1}$) of 1-MCP in the treatment chamber that resulted from using the calculated *k* values.

Table 3.5 Calculated vs. Experimental *k* values for *HDPE* at the different RH, initial 1-MCP concentrations and ratios ($kg/m^3$) tested.

| RH | Ratio | 1-MCP (μL $L^{-1}$) | k calc | SSE |
|---|---|---|---|---|
| 50 | 4 | 10 | 0.005306 | 0.0037 |
| | 4 | 20 | 0.002653 | 0.0075 |
| | 8 | 10 | 0.010612 | 0.0171 |
| | 8 | 20 | 0.005306 | 0.0014 |
| 80 | 4 | 10 | 0.006168 | 0.0229 |
| | 4 | 20 | 0.003084 | 0.0292 |
| | 8 | 10 | 0.012336 | 0.0273 |
| | 8 | 20 | 0.006168 | 0.0046 |
| 95 | 4 | 10 | 0.005027 | 0.0033 |
| | 4 | 20 | 0.002513 | 0.0005 |
| | 8 | 10 | 0.010053 | 0.0060 |
| | 8 | 20 | 0.005027 | 0.0040 |

Table 3.6 Calculated vs. Experimental *k* values for *corrugated board* at the different RH, initial 1-MCP concentrations and ratios ($kg/m^3$) tested.

| RH | Ratio | 1-MCP (μL $L^{-1}$) | k calc | SSE |
|---|---|---|---|---|
| 50 | 4 | 10 | 0.009645 | 0.0058 |
| | 4 | 20 | 0.004822 | 0.0012 |
| | 8 | 10 | 0.019289 | 0.0013 |
| | 8 | 20 | 0.009645 | 0.0080 |
| 80 | 4 | 10 | 0.053245 | 0.0300 |
| | 4 | 20 | 0.026622 | 0.0714 |
| | 8 | 10 | 0.106489 | 0.0490 |
| | 8 | 20 | 0.053245 | 0.0043 |
| 95 | 4 | 10 | 0.045300 | 0.0039 |
| | 4 | 20 | 0.022650 | 0.0137 |
| | 8 | 10 | 0.090600 | 0.0648 |
| | 8 | 20 | 0.045300 | 0.0111 |

These results confirm that the exponential model $C_t = C_0e^{-kt}$ is an excellent fit to the decreasing concentration of 1-MCP observed over time. The SSE values observed from Tables 3.5 and 3.6 suggest that there was good agreement between experimental and calculated concentrations of 1-MCP in the treatment chamber, which suggests that expression (6) provides a good estimator for the constant *k* values. Deviations between the experimental and calculated results were probably more due to experimental error than model error.

Calculated *k* values were substituted into expression (1) and the adequacy of the mathematical model for each given ratio of mass of corrugated board or HDPE (kg) per unit volume ($m^3$) of airspace in the treatment chamber, relative humidity and initial concentration, was tested by plotting the calculated 1-MCP concentration along with the experimental data collected versus time. Figures in Appendix C illustrate the results obtained.

As observed in figures 3.6 to 3.17, the loss of 1-MCP in the presence of corrugated board occurred more readily during the first 9 hours of the treatment period. The mechanism by which 1-MCP decreased in the presence of corrugated board is not yet known. It is possible, that 1-MCP is absorbed by glucose-based compounds in the plant cell walls. The α-1,4 glycosidic structure of cellulosic microfibrils has a cavity roughly similar in size to the cyclodextrin used in the SmartFresh® formulation (Carpita and McCann, 2000; cited by Vallejo and Beaudry, 2004).

Understanding diffusion is important in papermaking and end uses of paper and board. Presently, there is no general analytical model that can accurately predict the transport properties of fibrous composite structures such as paper and paperboard (Ramaswamy and Ramarao, 2004). Initially an attempt was made to model diffusion of 1-MCP through paperboard based on one-dimensional diffusion theory (please see Appendix B). This model failed to explain the actual behavior of MCP in the presence of corrugated board.

Paper and paper board are complex three dimensional layered structures of interconnected pores and cellulose fibers. Therefore, it is reasonable to expect that 1-MCP might penetrate into the bulk material and interact with it.

In terms of fundamental mechanisms, transport properties of paper are inherently related to the resistance offered by the three dimensional structure (Ramaswamy and Ramarao, 2004). Porosity (ratio of void volume to total volume), for instance, is known to effect permeation of ethylene oxide, a gas commonly use to sterilize medical devices packaged in paper pouches (Twede and Selke, 2004).

There might be several reasons to the decrease of 1-MCP concentration over time at different relative humidities, one of the reasons could be the effect of RH on changes in the structure of paper. Cellulose fibers are hygroscopic in nature, swelling of cellulose fibers in paperboard during moisture uptake might alter the fiber diameter.

There is not generally accepted explanation for the swelling behavior of fibers in paperboard. It has been suggested that the moisture content of paper

and paperboard is highly influenced by capillary condensation (Parker et al., 2006). Capillary condensation in the fiber walls is not significant at RH lower than 80%, but at RH conditions higher than 80% moisture is directly adsorbed by the mechanism of capillary condensation (Parker et al., 2006).

Interestingly, it has been reported that fibers are almost impermeable at relative humidities below 58%, but at higher relative humidities pores as well as fibers will behave as permeable media (Nilsson, 1993).

It follows, therefore, that as the RH increases (>80%) the fiber swelling will result in an increase of fiber diameter, while at the same time the pore space is opened up. This indicates that the molecules of 1-MCP gas diffusing through the paperboard might encounter a more open structure, easier to penetrate, and interact with it (Ramaswamy and Ramarao, 2004).

Furthermore, paper fibers have been traditionally treated as hollow cylindrical objects, but in reality their internal structure is very complex with many micro-fibrils, then the probability of interactions occurring inside the fibers cannot be ignored.

In addition to the structure parameters (porosity, fiber-void interfacial area, and pore size) discussed above, tortuosity is also important. Tortuosity is defined as the ratio of the actual length of the capillary to the straight line (or the shortest length) length of the capillary. In porous materials such as paper and paperboard, the inter-fiber capillaries can be expected to be highly tortuous (Ramaswamy and Ramarao, 2004). It has been suggested that it is also possible that shallow pores between almost parallel flat fiber surfaces act as

traps inside which the gas molecules have to bounce for a long time before escaping with a qualitative effect similar to that of sorption (Hellén et al., 2002).

The effect of tortuosity might be more evident at low concentrations of 1-MCP than at high concentrations as fewer molecules are available in the headspace of the treatment chamber to be trapped in these tortuous channels through the sheet, causing the initial concentration to decrease faster. Similarly this might explain why at higher ratios of corrugated board the initial concentration of 1-MCP is reduced more readily.

Although the method presented in this research is based on some assumption, idealization, and limitations, it provides a protocol of practical significance if applied carefully.

## 3.4 Conclusions

The concentration of 1-MCP declined in the presence of the materials tested, and the rate and amount of 1-MCP gas removed from the chamber was dependent on the type of material. The average percentage loss for HDPE and wood was between 10-12% at all conditions tested, while for corrugated fiberboard it ranged from 12% to 94%.

The reduction in mass of 1-MCP over time seems to follow a behavior that can be fitted by the exponential model $C_t = C_0 e^{-kt}$. The rate at which 1-MCP gas was removed from the headspace of the treatment chamber is proportional to the initial mass of 1-MCP in the treatment chamber and to treatment time. It is also apparently proportional to the mass of material in the headspace of the treatment chamber, and is proportional to the mass of moisture (RH) present in the treatment chamber.

The mechanism to explain loss of 1-MCP in the presence of corrugated board is not yet known, however, transport properties of paper and paperboard are known to be inherently related to the resistance offered by the three dimensional structure of paper materials, and are likely affected by characteristics such as porosity, fiber-void interfacial area (surface area), pore size distribution, and structural tortuosity.

**Literature cited**


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# APPENDICES

# APPENDIX A

## 1-MCP CALIBRATION CURVE

A 1-butene gas standard was used to determine the concentration of 1-MCP. To create a 10 μL $L^{-1}$ 1-butene standard, 43 μL of pure 1-butene (Matheson Gas Products, Chicago, IL), were injected into a 4.3 L specially-made glass chamber fitted with a Mininert valve (Supelco, Bellefonte, PA). It was assumed that the response factor for 1-MCP (molecular weight of 54.09 g/mol) and 1-butene (molecular weight of 51 g/mol) would be similar (Vallejo and Beaudry, 2006). A standard curve for 1-butene was prepared for concentrations ranging between 1 to 10 μL $L^{-1}$ and it is shown in figure A1. The solid line represents the regression line fitted using experimental data (dots).

As observed, the equation that adequately describes the relationship between 1-MCP and 1-butene is linear in the range of 1 to 10 μL $L^{-1}$.

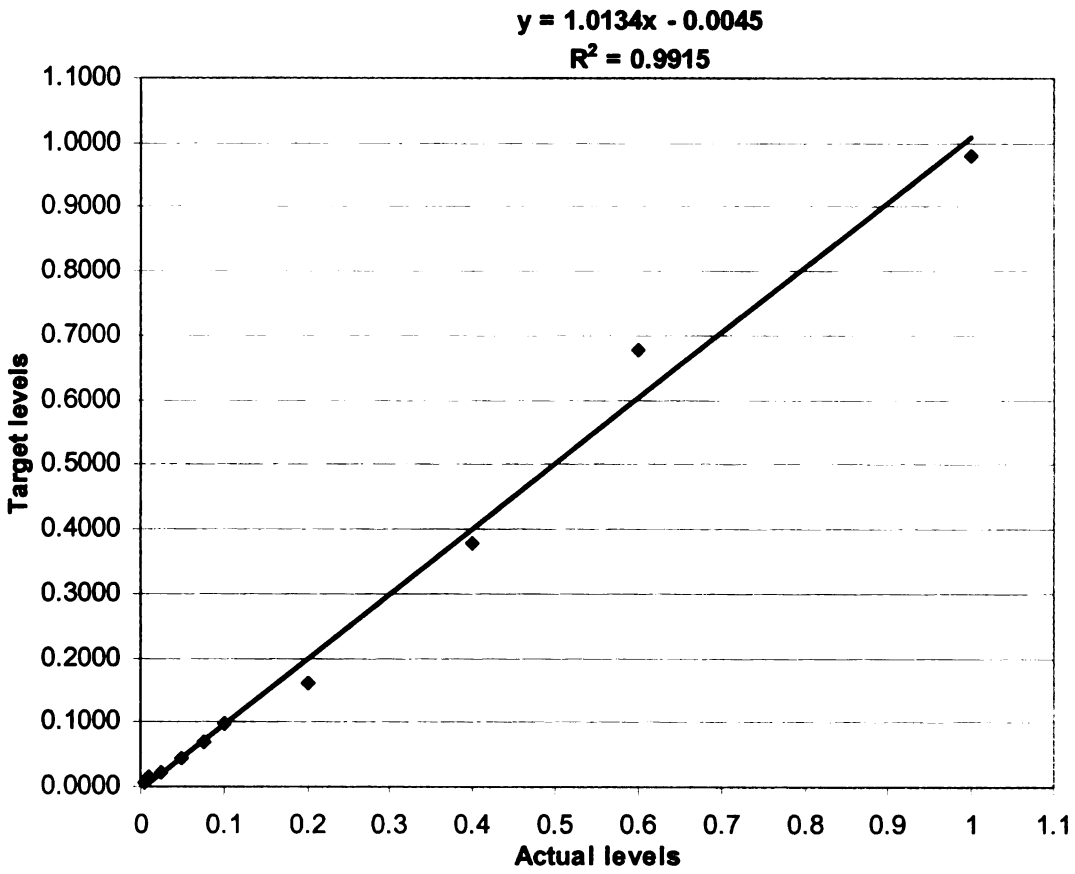


Figure A1. 1-MCP calibration curve prepared using 1-butene: correlation between target and actual levels of 1-MCP.

# APPENDIX B

# MODEL TO DESCRIBE PERMEABILITY OF 1-METHYLCYCLOPROPENE THROUGH PAPERBOARD

## Diffusion theory basis used for this model

In many packaging applications, the permeability of a polymer membrane can be described by the following expression:

$$P = DS \qquad (1)$$

where P is the permeability coefficient, D is the Fickian diffusion coefficient, and S is the Henry's Law solubility coefficient. The permeability coefficient (P) is the steady-state transport rate of permeant molecules through a polymer membrane of unit area per unit of thickness and driving force, while the diffusion coefficient (D) represents how fast the permeant molecules move through the polymer bulk phase, and the solubility coefficient (S) is a measure of the mass of permeant molecules sorbed by a unit of polymer mass per unit of partial pressure (Barr, Giacin and Hernandez, 2000).

The simplest solutions for diffusion-controlled behavior usually correspond to assuming a semi-infinite medium with a motionless flat interface, initial uniform concentration, without reactions, and transport controlled by diffusion (Frade, 1997).

For situations in which Fick's law with a constant diffusion coefficient applies, the unidirectional flux through a membrane is given in equation (2).

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} \qquad (2)$$

where *C* is the concentration of the diffusing penetrant, *x* is the direction in which the diffusion takes place, and *t* the time (Crank, 1975).

Henry's law describes the solubility of a compound present in a gas phase that is in contact with a solid phase; it states that the concentration of a solute gas in the solid phase is directly proportional to the concentration (or partial pressure) of that compound in the contacting gas phase.

For situations in which Henry's law is obeyed the sorption expression through a membrane is given in equations (3).

$$c_i = Sp_i \qquad (3)$$

where $c_i$ is the concentration of the gas in the solid phase, S the solubility coefficient of the substance at equilibrium, and $p_i$ the partial pressure of the gas in the contacting gas phase (Selke, Culter, and Hernandez, 2004).

## Materials and Methods

A concentrated source of 1-MCP gas was created by adding 25 mL of distilled water to a 0.47-L glass jar containing 0.32 g of Smart-Fresh (AgroFresh, Springhouse, PA), with an active ingredient concentration of 3.3%.

A gas standard of 1-butene was used to calculate the concentration of 1-MCP in the headspace of the stock jar. To create a 10 μL $L^{-1}$ 1-butene standard, 43 μL of pure 1-butene was injected into a 4.3-L specially made glass chamber fitted with a Mininert valve. It was assumed that the response factor for 1-MCP and 1-butene were similar.

The concentration of 1-butene and 1-MCP in the stock preparation was quantified by gas chromatography (Carle Series 100 AGC) with an oven temperature of 140°C on a 2 m (length) x 2 mm (inner diameter) column packed with 60/80 Chromosorb OV-103 (Alltech Associates Inc., Deerfield, IL) fitted with a FID. The flow rates for the carrier gas (He), H2, and air were approximately 50, 50, and 200 mL $min^{-1}$, respectively. The actual concentration of 1-MCP in the stock gas was calculated.

Then a volume of 1-MCP gas from the stock gas was injected into an empty glass jars (with a headspace volume of 1,000 mL) sufficient to obtain a target gas concentration of 500 μL $L^{-1}$.

The jar was fitted with a rubber septum by drilling a hole on one of the side walls. Kraft paper samples with a thickness of 17 mil (0.04318 cm) and a diameter of 2.2 cm were cut and previously conditioned at 20°C, 90% RH for 24 h. The jar mouth was covered with the conditioned paperboard; the paper lid was tight against the mouth edges using a threaded metal ring.

The jar, which will be referred to as *Chamber 1*, was put inside a larger chamber – *Chamber 2* (a high density polyethylene bucket with clamp closures on the top) with a headspace volume of 20 L at 20°C, 95% RH. The relative humidity was achieved by pouring 25 mL of water in chamber 2. This second chamber was fitted with a rubber septum on the top and tight sealed.

The concentration of 1-MCP in the headspace of Chamber 2 was monitored by gas chromatography, gas samples were taking at intervals of 60 s for the first 5 min and right afterwards time intervals were increased from 1 min to 5 minutes until equilibrium was reached; this happened 135 minutes after injecting concentrated 1-MCP in chamber 1.

The figure below illustrates the setup of the experiment:

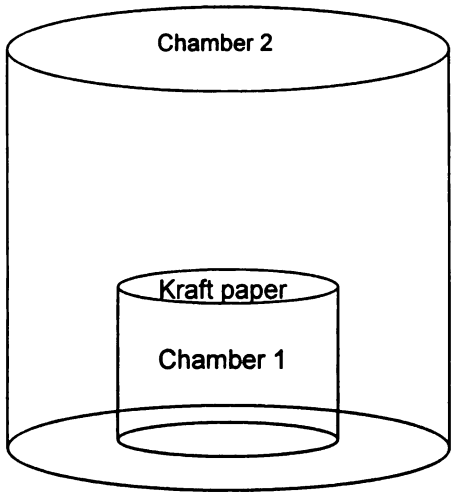


Figure B1. Setup of an experiment to determine the solubility of 1-MCP through paperboard.

**Results:**

Results are summarized in tables B1 & B2.

Table B1. Concentration of 1-MCP (g/cc) in Chamber 2 after diffusing through a paperboard membrane – Replicate 1.

| Time (m) | Time (s) | [1-MCP] in μL $L^{-1}$ | [1-MCP] in g/cc |
|---|---|---|---|
| 0 | 0 | 0 | 0.00E+00 |
| 1 | 60 | 2.9 | 6.99E-09 |
| 2 | 120 | 3.5 | 8.43E-09 |
| 3 | 180 | 3.5 | 8.43E-09 |
| 4 | 240 | 4.05 | 9.76E-09 |
| 5 | 300 | 4.65 | 1.12E-08 |
| 7.5 | 450 | 5.1 | 1.23E-08 |
| 10 | 600 | 5.95 | 1.43E-08 |
| 15 | 900 | 6.25 | 1.51E-08 |
| 20 | 1200 | 7.1 | 1.71E-08 |
| 25 | 1500 | 7.9 | 1.90E-08 |
| 30 | 1800 | 8.45 | 2.04E-08 |
| 40 | 2400 | 9.18 | 2.21E-08 |
| 50 | 3000 | 10.11 | 2.44E-08 |
| 60 | 3600 | 10.23 | 2.46E-08 |
| 70 | 4200 | 10.58 | 2.55E-08 |
| 80 | 4800 | 11.05 | 2.66E-08 |
| 90 | 5400 | 11.5 | 2.77E-08 |
| 100 | 6000 | 12.2 | 2.94E-08 |
| 110 | 6600 | 12.55 | 3.02E-08 |
| 120 | 7200 | 12.56 | 3.03E-08 |
| 130 | 7800 | 12.56 | 3.03E-08 |
| 140 | 8400 | 12.56 | 3.03E-08 |

Table B2. Concentration of 1-MCP (g/cc) in Chamber 2 after diffusing through a paperboard membrane – Replicate 2.

| Time (m) | Time (s) | [1-MCP] in μL $L^{-1}$ | [1-MCP] in g/cc |
|---|---|---|---|
| 0 | 0 | 0 | 0.00E+00 |
| 1 | 60 | 0.43 | 1.04E-09 |
| 2 | 120 | 1.51 | 3.64E-09 |
| 3 | 180 | 2.36 | 5.69E-09 |
| 4 | 240 | 2.79 | 6.72E-09 |
| 6 | 360 | 4.3 | 1.04E-08 |
| 9 | 540 | 6.07 | 1.46E-08 |
| 12 | 720 | 7.63 | 1.84E-08 |
| 15 | 900 | 9.25 | 2.23E-08 |
| 18 | 1080 | 10.65 | 2.57E-08 |
| 21 | 1260 | 11.83 | 2.85E-08 |
| 24 | 1440 | 12.74 | 3.07E-08 |
| 27 | 1620 | 13.87 | 3.34E-08 |
| 30 | 1800 | 14.62 | 3.52E-08 |
| 33 | 1980 | 14.95 | 3.60E-08 |
| 39 | 2340 | 16.02 | 3.86E-08 |
| 42 | 2520 | 16.29 | 3.92E-08 |
| 45 | 2700 | 16.34 | 3.94E-08 |
| 48 | 2880 | 16.98 | 4.09E-08 |
| 51 | 3060 | 17.2 | 4.14E-08 |
| 54 | 3240 | 17.2 | 4.14E-08 |
| 57 | 3420 | 17.63 | 4.25E-08 |
| 60 | 3600 | 17.63 | 4.25E-08 |
| 70 | 4200 | 18.92 | 4.56E-08 |
| 80 | 4800 | 18.92 | 4.56E-08 |
| 95 | 5700 | 18.92 | 4.56E-08 |
| 110 | 6600 | 19.14 | 4.61E-08 |
| 125 | 7500 | 18.92 | 4.56E-08 |
| 140 | 8400 | 19.14 | 4.61E-08 |

As observed in Table A2, steady state was reached 1 h and 10 min after injection with 1-MCP. The concentration of 1-MCP in the headspace of chamber 2 was monitored for an additional 18 h to verify an airtight seal in chamber 2:

- after 1 h and 30 min the concentration of 1-MCP remained constant (this is no change from steady state),
- after 6 hours the concentration of 1-MCP declined slightly by 1%,
- after 18 hours the concentration of 1-MCP in the headspace of chamber 2 declined by 5%.

These results suggest that during the first 7 h of the experiment (70 min of non-steady state plus 6 h after reaching steady state) losses of 1-MCP gas from the headspace of Chamber 2 were not significant.

However, the 5% loss of 1-MCP detected during the last measurement (18 h after reaching steady state) might be due to either minor leaks in the system or to reaction of the 1-MCP molecules with the paperboard, which could have trapped (physically or chemically bound) some of them.

Several methods have been described for measuring the mass transfer characteristics of polymer films, including a gravimetric technique and an isostatic permeation procedure (Barr, Giacin and Hernandez, 2000).

From the data collected we attempted to calculate the diffusion and solubility coefficients. The calculated results obtained in the course of this work are summarized below.

For constant diffusivity, the mass balance for 1-MCP in the paperboard reduces to expression (2).

Only in the simplest cases of sorption or desorption from a plane sheet with constant surface concentration, is it possible to derive formal mathematical solutions for the diffusion coefficient of this kind. Finite difference methods must be used to obtain numerical solutions (Crank, 1952) for general cases.

Expressions 2 and 3 presented above must be defined quantitatively before the numerical work can proceed. For more quantitative information, we resorted to calculation.

The initial conditions of our experiment are

$$\text{At } t = 0: C_1 = C_0;\ C_2 = 0,\ C(x,0) = 0 \qquad (3)$$

where $C_0$ is the initial concentration of 1-MCP in chamber 1.

Figure B2 below illustrates the variables involved.

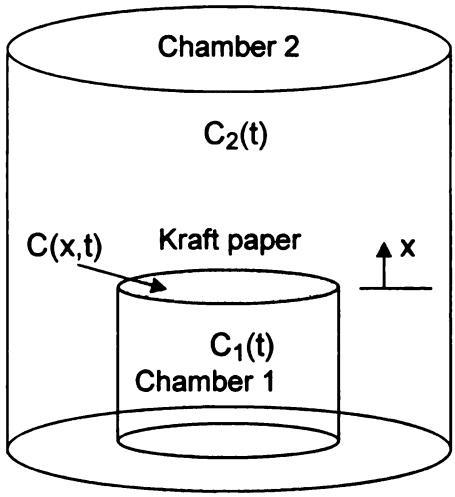


Figure B2. Variable in the experiment to determine the solubility of 1-MCP through paperboard.

The boundary conditions of our experiment are

$$\text{At } x = 0: \; C(0,t) = k\, C_1(t) \qquad (4)$$

$$\text{At } x = 0: \; \frac{\partial C}{\partial x} = \frac{V_1}{DAk} \frac{\partial C}{\partial t} \qquad (5)$$

$$\text{At } x = w: \; \frac{\partial C}{\partial x} = -\frac{V_2}{DAk} \frac{\partial C}{\partial t} \qquad (6)$$

where is $w$ the thickness of the material specimen (0.0004318 m), $V_1$ is the volume in chamber 1 (0.001 $m^3$), $V_2$ is the volume in chamber 2 (0.02 $m^3$), A is the area of the membrane (0.00038 $m^2$), and $k$ is related to the solubility of 1-MCP in the paper.

Equation (5) comes from a mass balance for 1-MCP in the headspace of chamber 1. The rate at which 1-MCP enters the surface x=0 of the paperboard is given by Fick's law: $-DA(\partial C/\partial x)$. The rate at which 1-MCP is removed from the headspace is given by $-d(C_1V_1)/dt$.

Equating these two rates and using $\frac{dC_1}{dt} = \frac{1}{k}\frac{\partial C}{\partial t}$ from (4) gives (5).

A similar argument yields (6).

To relate the constant k to solubility, we know from the ideal gas law that:

$$p_i = \frac{nRT}{V} \qquad (7)$$

where

$p_i$ = partial pressure of 1-MCP (Pa) in chamber 2

n = number of moles of 1-MCP

R = molar gas constant (8.314 $m^3$ Pa $mole^{-1}$ $K^{-1}$)

T = temperature (293K for our experiment)

V = volume (in liters)

n can also be expressed as: $n = \frac{cV}{M}$ (8)

where

c = concentration of 1-MCP in chamber 2

V = volume (liters)

M = molecular weight (54.09 g/mole)

By substituting in expression (7), we get:

$p_i = \frac{RTC}{V} = 45{,}040\ C$

Substituting in expression (4) the concentration of 1-MCP in the paper is:

$$C_{paper} = 45{,}040\ C_{headspace}\ S \qquad (9)$$

Since the product of 45,040 and the solubility coefficient *S* is a constant value, equation (9) can be expressed as

$$C_{paper} = k\ C_{headspace} \qquad (10)$$

where k = 45,040S.

**Prediction of the permeability coefficient**

It can be shown that the partial differential equation given by expression (2) can be solved by the separation of variables method (Arfken, 1985); that equation and both boundary conditions of our experiment are satisfied by the following expression[1]:

$$C(k,t) = g_0 + \sum_{i=1}^{\infty} g_i[\cos(\beta_i x / w) - R_1 \beta_i \sin(\beta i\, x / w)]e^{-\beta i\, Dt / w^2} \quad (11)$$

where the eigenvalues $\beta_i$ satisfy

$$[\beta i^2 - \frac{1}{R_1 R_2}] \tan \beta_i = [\frac{1}{R_1} + \frac{1}{R_2}] \beta_i \quad (12)$$

with

$$R_1 = \frac{V_1}{kAw} \quad \text{and} \quad R_2 = \frac{V_2}{kAw} \quad (13)$$

There are an infinite number of eigenvalues satisfying

$$(i - 1)\pi < \beta_i < (i - \tfrac{1}{2})\pi \quad (14)$$

Since the functions $\cos(\beta_i x / w) - R_1 \beta_i \sin(\beta i\, x / w)$ are not orthogonal on (0,w), the only way to determine the g's is by collocation.

Microsoft® GW-BASIC® was used to create a program to solve for the eigenvalues and the g's by collocation. The program is shown below.

[1] Internal communication from Dr.Gary Burgess, Professor at the School of Packaging, MSU; January 31, 2007.

```
10 '********** experimental data **************
20 ND=20 : DIM TIME(ND),CONC(ND) 'time vs conc (sec vs kg/m^3)
30 FOR I=1 TO ND : READ TIME(I),CONC(I) : NEXT I
40 DATA (insert data here)
80 W=.0004318 : A=.004536 'thickness (m) & area (m^2)
90 V1=.001 : C0=.0007612 'left vol (m^3) & initial concentration (kg/m^3)
100 V2=.02 'right volume (m^3)
110 CF=45040! 'Henry's Law conversion factor
120 D=.0000004 : S=.000006 'diffusion coeff (m^2/sec) & solubility (kg/m^3-Pa)
130 C0=CONC(ND)*(V1+V2+CF*S*A*W)/V1 'corrected c0
131 'PRINT C0 : STOP
140 '************** eigenvalues ****************
150 R1=V1/(CF*S*A*W) : R2=V2/(CF*S*A*W)
160 NEV=10 : DIM BETA(NEV)
170 FOR I=1 TO NEV : BETA(I)=(I-1)*3.141592654#+.0001
180 DB=.1 : FOR M=1 TO 6
190 Y=(BETA(I)^2-1/(R1*R2))*TAN(BETA(I))-(1/R1+1/R2)*BETA(I)
200 IF Y<0 THEN BETA(I)=BETA(I)+DB : GOTO 190
210 BETA(I)=BETA(I)-DB : DB=DB/10 : NEXT M
220 'PRINT "beta"I;"=";BETA(i);"     error in y="Y
230 NEXT I
240 '************* collocation **************
250 N=NEV+1 : DIM C(N,N+1),G(N)
260 FOR I=1 TO N : C(I,1)=1 : C(I,N+1)=0 : NEXT I
270 FOR J=1 TO N+1 : C(1,J)=1 : NEXT J
280 FOR I=2 TO N : FOR J=2 TO N
290 C(I,J)=COS(BETA(J-1)*(I-1)/NEV)-R1*BETA(J-1)*SIN(BETA(J-1)*(I-1)/NEV)
300 NEXT J : NEXT I
310 FOR I=1 TO N 'solve system of equations
320 PVT=I : FOR K=I+1 TO N : IF ABS(C(K,I))>ABS(C(PVT,I)) THEN PVT=K :
NEXT K
330 FOR J=I TO N+1 : CHG=C(I,J) : C(I,J)=C(PVT,J) : C(PVT,J)=CHG : NEXT J
340 FOR K=1 TO N : IF K=I THEN 360
350 FOR J=I+1 TO N+1 : C(K,J)=C(K,J)-C(K,I)*C(I,J)/C(I,I) : NEXT J
360 NEXT K : NEXT I
370 FOR K=1 TO N : G(K)=C(K,N+1)/C(K,K) : NEXT K
380 'FOR K=1 TO N : PRINT K,G(K) : NEXT K : STOP
390 '************** solution ******************
400 PRINT "time          c2-exact          c2-exp"
410 FOR I=1 TO ND
420 C2=G(1) : FOR J=1 TO NEV
430 Z=EXP(-BETA(J)^2*D*TIME(I)/W^2)
440 C2=C2+G(J+1)*(COS(BETA(J))-R1*BETA(J)*SIN(BETA(J)))*Z
450 NEXT J : C2=C2*C0 : PRINT TIME(I),C2,CONC(I)
460 NEXT I
470 LIST 120 Ok
```

Identifying the best pair of values for D and S was done using the technique of least squares regression. The best fit values of D and S were the ones that minimized the sum of squares of the errors (SSE) between the experimental concentration of 1-MCP in chamber 2 and the predicted concentrations using (11).

Tables B3 and B4 show the results of a search for D and S.

Table B3. Best values of D and S within different ranges, using experimental data from Replicate 1.

| Range of D & S | Best D | Best S | SSE | P |
|---|---|---|---|---|
| FOR D=.000001 TO .000002 STEP .0000001<br>FOR S=.0000015 TO .000008 STEP .0000005 | 2.000E-06 | 7.500E-06 | 2.442228 | 1.500E-11 |
| FOR D=.000001 TO .000002 STEP .0000001<br>FOR S=.0000085 TO .000015 STEP .0000005 | 2.000E-06 | 9.000E-06 | 2.184647 | 1.800E-11 |
| FOR D=.0000015 TO .0000035 STEP .0000005<br>FOR S=.0000015 TO .000008 STEP .0000005 | 3.500E-06 | 5.500E-06 | 2.179936 | 1.925E-11 |
| FOR D=.0000025 TO .0000035 STEP .0000001<br>FOR S=.0000015 TO .000008 STEP .0000005 | 2.800E-06 | 6.500E-06 | 2.170954 | 1.820E-11 |

Table B4. Best values of D and S within different ranges, using experimental data from Replicate 2.

| Range of D & S | Best D | Best S | SSE | P |
|---|---|---|---|---|
| FOR D=.000001 TO .000002 STEP .0000001<br>FOR S=.0000015 TO .000008 STEP .0000005 | 2.000E-06 | 7.500E-06 | 1.539987 | 1.500E-11 |
| FOR D=.000001 TO .000002 STEP .0000001<br>FOR S=.0000085 TO .000015 STEP .0000005 | 1.400E-06 | 1.300E-05 | 0.106572 | 1.820E-11 |
| FOR D=.0000015 TO .0000035 STEP .0000005<br>FOR S=.0000015 TO .000008 STEP .0000005 | 3.000E-06 | 6.000E-06 | 0.108755 | 1.800E-11 |
| FOR D=.0000025 TO .0000035 STEP .0000001<br>FOR S=.0000055 TO .0000075 STEP .0000001 | 2.600E-06 | 7.000E-06 | 0.103756 | 1.820E-11 |

The units of *S* were kg $m^{-3}$ $Pa^{-1}$. The units of D were $m^2$ $s^{-1}$. Finally, the units of P were kg m $m^{-2}$ $s^{-1}$ $Pa^{-1}$.

As observed in Tables 3 & 4, the best values for D and S during the first test were $2.8x10^{-6}$ and $6.5x10^{-6}$, respectively. The best values for D and S during the second test were $2.6x10^{-6}$ and $7.0x10^{-6}$, respectively.

The permeability coefficient was calculated from expression (1). The obtained value was $1.82x10^{-11}$ kg m $m^{-2}$ $s^{-1}$ $Pa^{-1}$ for both tests.

**Model validation**

After identifying the best values for D and S, the next step was to validate the model using different concentrations of 1-MCP and relative humidities. Materials and methods were identical to the ones presented above; concentrations tested were 100, 200 and 500 µL $L^{-1}$, at relative humidities of 10 and 95%.

A glass system device was designed to reduce experimental error and is shown in figure B3 below.

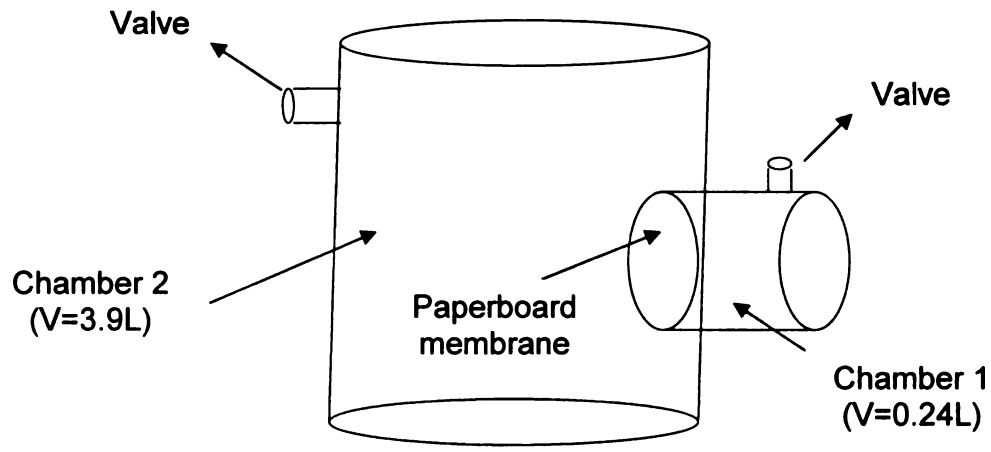


Figure B3. Glass system designed to validate the model to describe permeability of 1-MCP through paperboard.

The concentration of 1-MCP in the headspace of Chamber 2 was monitored by gas chromatography, gas samples were taking at intervals of 120 s for the first 5 min, and then to 3 minutes until equilibrium was reached. Figure B4 illustrates results.

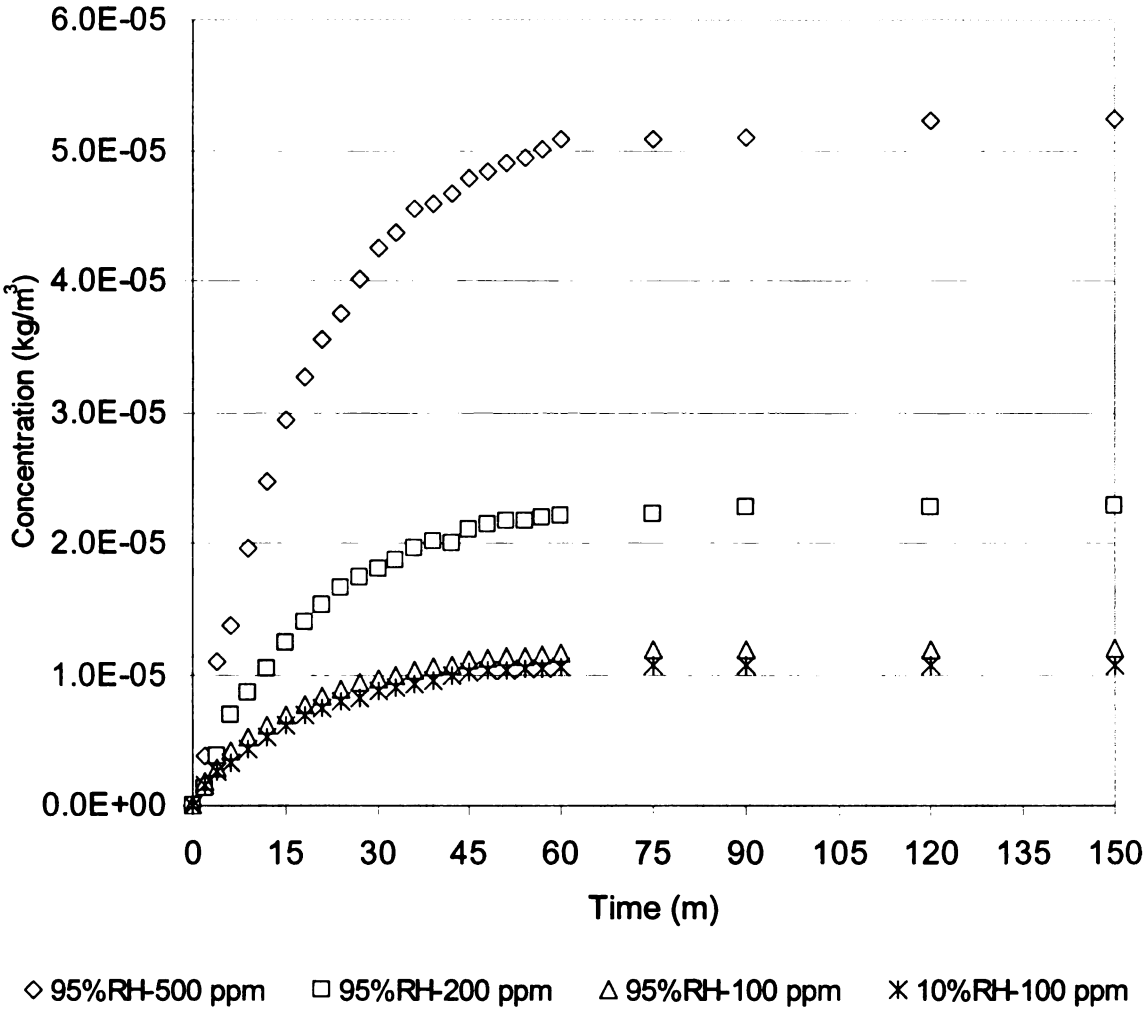


Figure B4. Concentration of 1-MCP on chamber 2 after diffusing through a paperboard membrane at different relative humidities and concentrations of 1-MCP

Following the procedure developed for our model, we estimated the solubility (S), diffusion (D) and permeability (P) coefficients at the different conditions tested (Table B3). The units of *S* were kg $m^{-3}$ $Pa^{-1}$. The units of D were $m^2$ $s^{-1}$. Finally, the units of P were kg m $m^{-2}$ $s^{-1}$ $Pa^{-1}$.

Table B5. Predicted values of coefficients S, D and P for 1-MCP through paperboard.

| Treatment | Replicate | Best D | Best S | SSE | P = DS |
|---|---|---|---|---|---|
| 95%RH-500 μL $L^{-1}$ | 1 | 2.50E-07 | 3.70E-04 | 0.383665 | 9.25E-11 |
| | 2 | 5.50E-07 | 1.51E-04 | 0.17968 | 8.31E-11 |
| | 3 | 4.50E-07 | 1.81E-04 | 0.353451 | 8.14E-11 |
| | Avg | 4.17E-07 | 2.34E-04 | | 8.57E-11 |
| | Std.Dev. | 1.53E-07 | 1.19E-04 | | 5.97E-12 |
| 95%RH-200 μL $L^{-1}$ | 1 | 2.50E-07 | 3.60E-04 | 0.138213 | 9.00E-11 |
| | 2 | 3.50E-07 | 2.59E-04 | 2.19E-02 | 9.06E-11 |
| | 3 | 1.50E-07 | 4.96E-04 | 5.51E-02 | 7.44E-11 |
| | Avg | 2.50E-07 | 3.72E-04 | | 8.50E-11 |
| | Std.Dev. | 1.00E-07 | 1.19E-04 | | 9.20E-12 |
| 95%RH-100 μL $L^{-1}$ | 1 | 3.50E-07 | 2.63E-04 | 2.89E-02 | 9.20E-11 |
| | 2 | 5.50E-07 | 1.68E-04 | 3.39E-02 | 9.24E-11 |
| | 3 | 5.50E-07 | 1.56E-04 | 8.34E-03 | 8.58E-11 |
| | Avg | 4.83E-07 | 1.96E-04 | | 8.91E-11 |
| | Std.Dev. | 1.15E-07 | 5.86E-05 | | 4.67E-12 |
| 10%RH-100 μL $L^{-1}$ | 1 | 5.50E-07 | 1.65E-04 | 1.74E-02 | 9.07E-11 |
| | 2 | 1.50E-07 | 5.33E-04 | 3.78E-02 | 8.00E-11 |
| | 3 | 6.50E-07 | 1.64E-04 | 2.64E-02 | 1.07E-10 |
| | Avg | 4.50E-07 | 2.87E-04 | | 8.54E-11 |
| | Std.Dev. | 2.65E-07 | 2.13E-04 | | 7.64E-12 |

## Discussion

Results from our model showed almost identical estimated values for the P coefficient regardless of the relative humidity or initial concentration, similar results were obtained for the values of D and S.

When comparing these results with the actual behavior of 1-MCP concentration observed in experiments conducted simultaneously with corrugated fiberboard boxes (made from the same Kraft paper used for our modeling experiments) in large treatment chambers we were able to determine that the proposed model was not adequate to explain the experimental results obtained from this later system.

The inhomogeneous structure of paper and board complicates the diffusion analysis. The average diffusion constant of a relatively thick sheet can be quite different from the diffusion constant of a thin sheet or a thin layer of a thick sheet (Hellen et al. 2002).

Furthermore, it has been reported that when sorption is significant, steady-state measurements of the diffusion constant combined with one-dimensional diffusion theory are not enough to predict the dynamic evolution of diffusion flux (Hellen et al. 2002).

A pore space diffusion model has been developed to simulate simultaneous diffusion in heterogeneous porous materials such as paper containing cellulose fibers and void spaces. A stochastic dynamic approach along with random walk simulation has been used to model simultaneous diffusion in the 3D matrix of cellulose fibers and pores. This model is suitable for simulating simultaneous diffusion in porous materials under a variety of conditions including low relative humidity where diffusion occurs predominantly through one medium (i.e. pore space) and high humidity where both mediums (i.e. fiber and pore spaces) are highly conductive (Ramaswamy and Ramarao, 2004).

Even though the existence of such models is recognized, their use is complex and calculations are time consuming. As an alternative, we decided to try an approach that would mimic commercial conditions, which is discussed in Chapter 3.

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## APPENDIX C

## COMPARISON OF EXPERIMENTAL AND ESTIMATED CONCENTRATION OF 1-MCP USING THE CALCULATED *k* VALUES

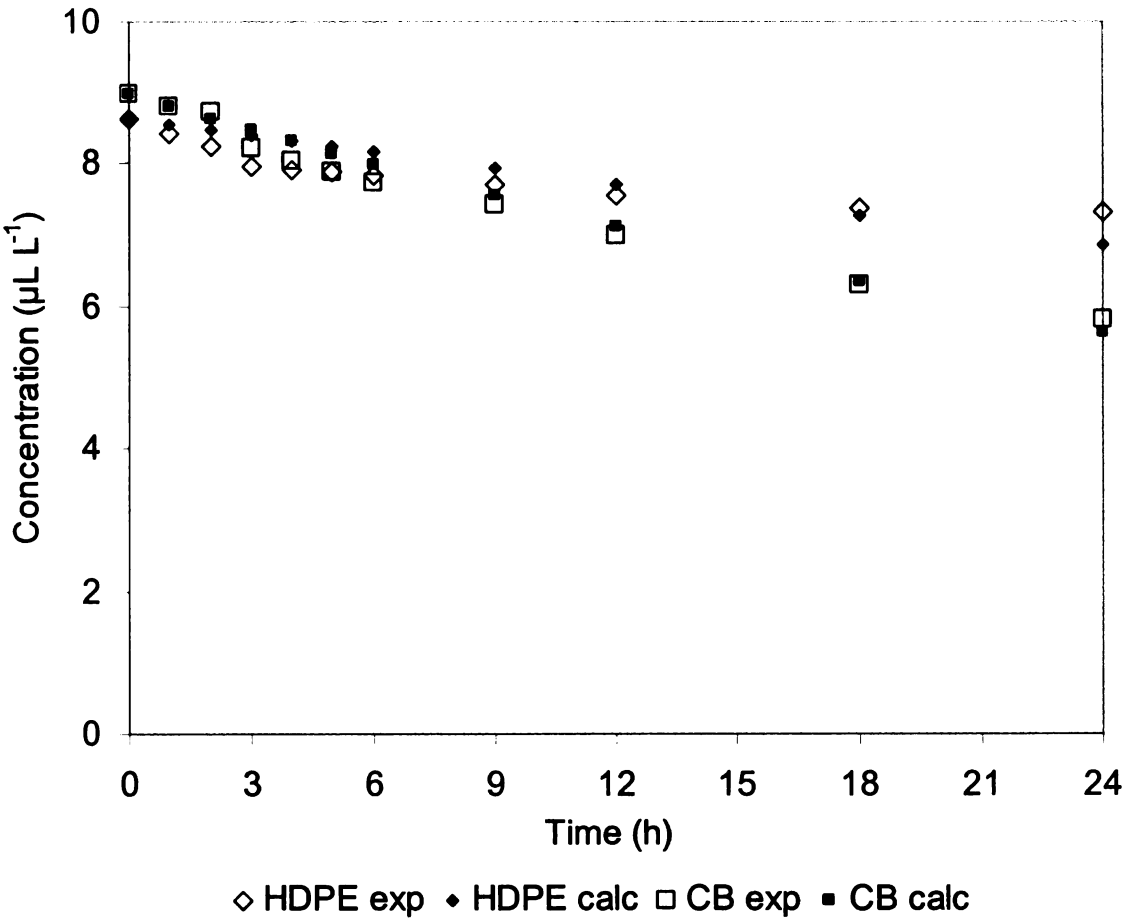


Figure C1. Comparison of experimental and estimated concentration of 1-MCP using the calculated k values (R = 8 kg/m$^3$, Co = 10 µL L$^{-1}$, 50%RH at 20°C).

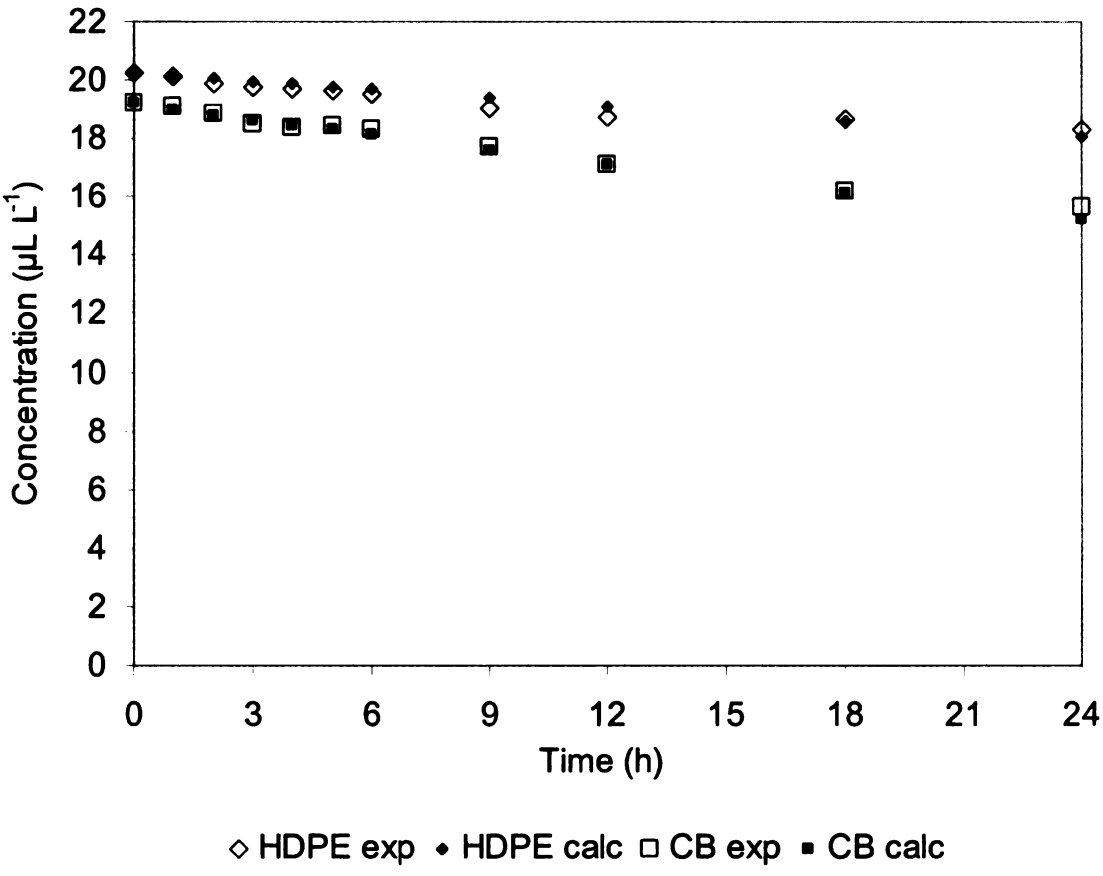


Figure C2. Comparison of experimental and estimated concentration of 1-MCP using the calculated k values (R = 8 kg/ $m^3$, Co = 20 µL $L^{-1}$, 50%RH at 20°C).

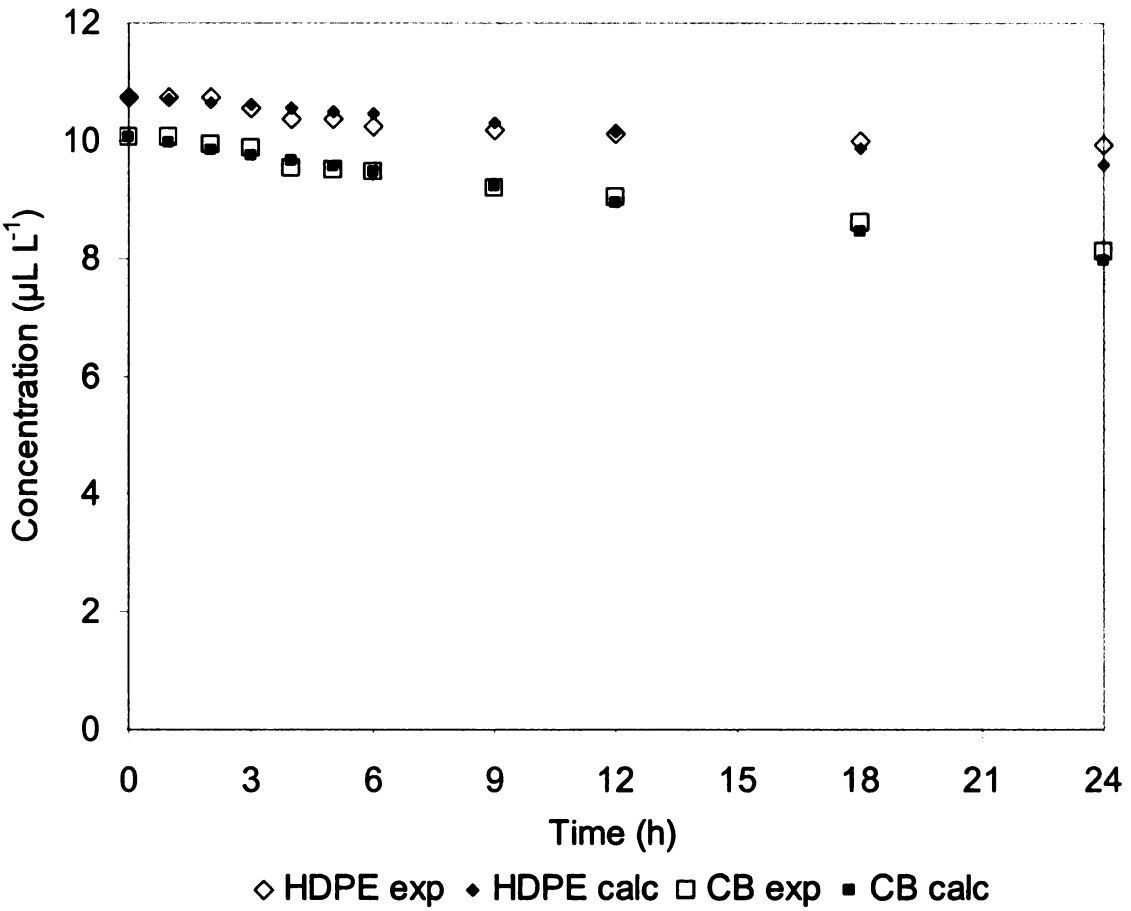


Figure C3. Comparison of experimental and estimated concentration of 1-MCP using the calculated k values (R = 4 kg/ $m^3$, Co = 10 µL $L^{-1}$, 50%RH at 20°C).

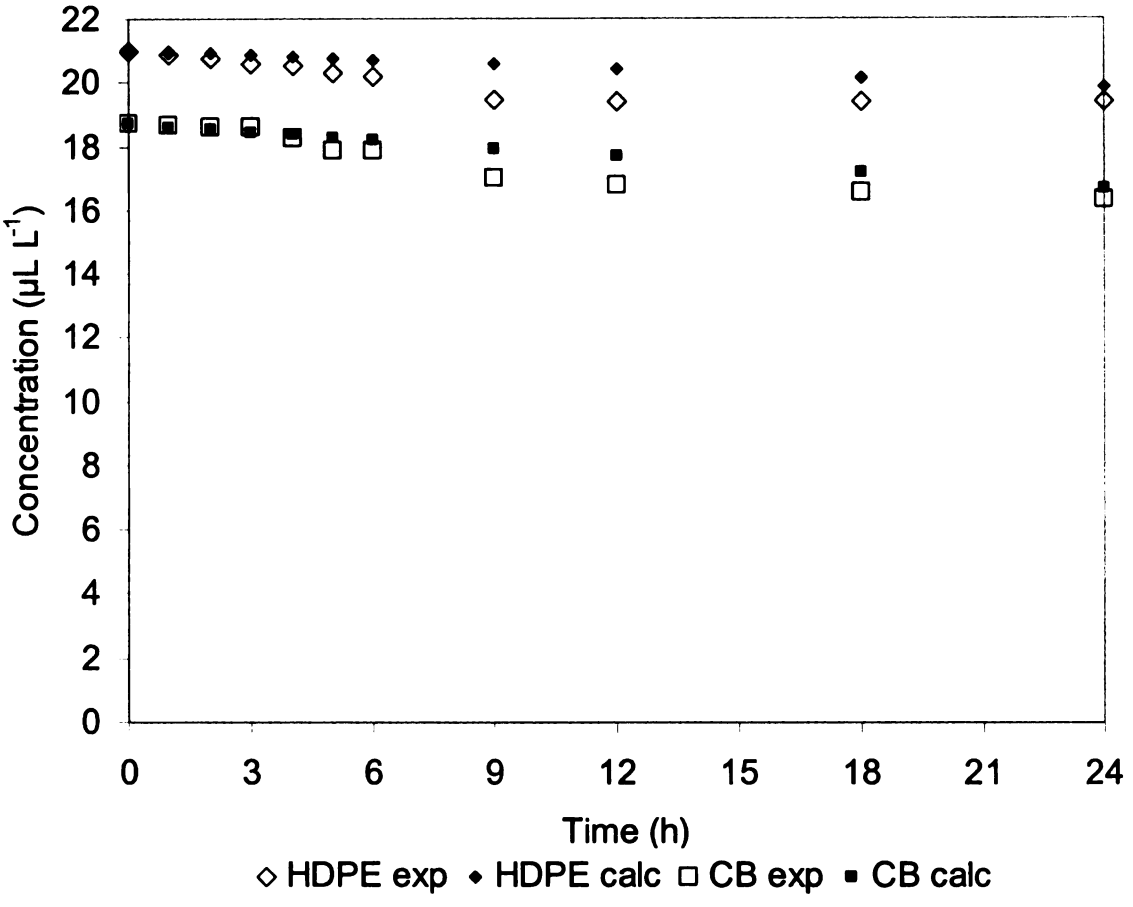


Figure C4. Comparison of experimental and estimated concentration of 1-MCP using the calculated k values (R = 4 kg/ $m^3$, Co = 20 µL $L^{-1}$, 50%RH at 20°C).

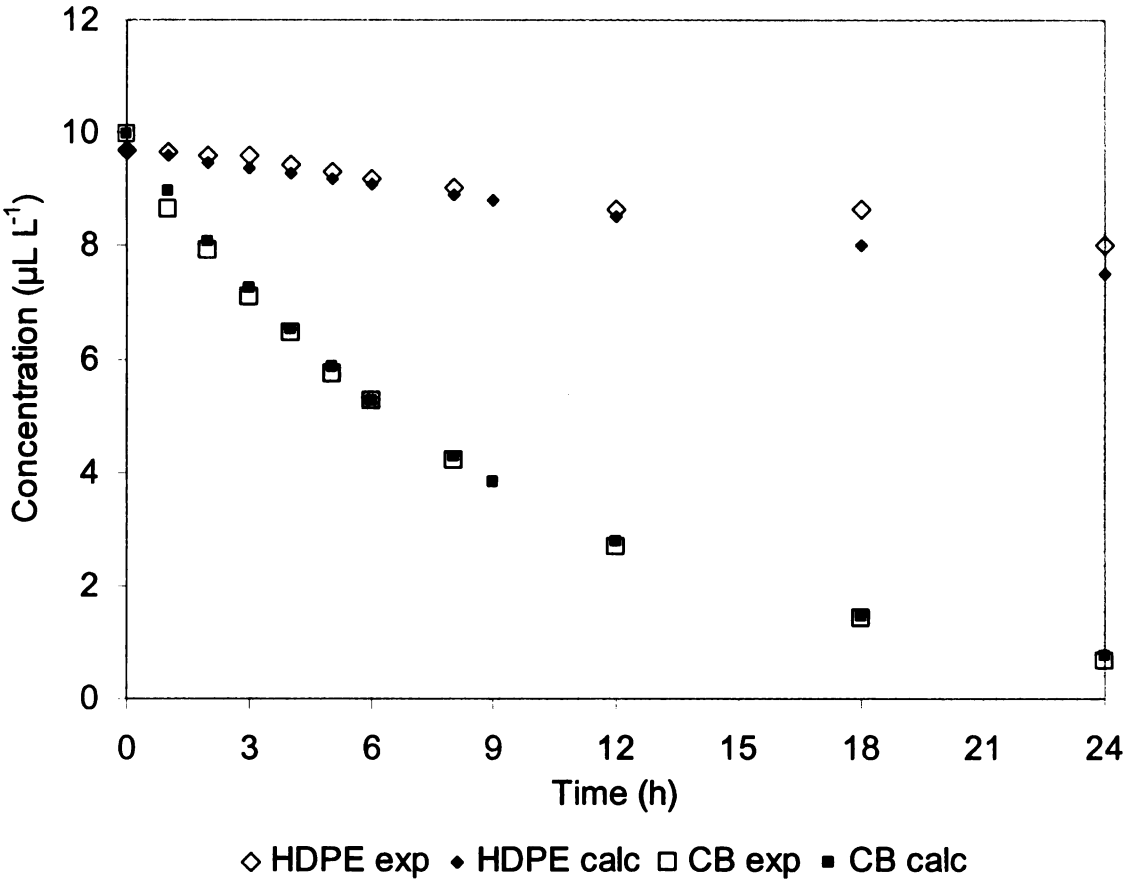


Figure C5. Comparison of experimental and estimated concentration of 1-MCP using the calculated k values (R = 8 kg/ $m^3$, Co = 10 µL $L^{-1}$, 80%RH at 20°C).

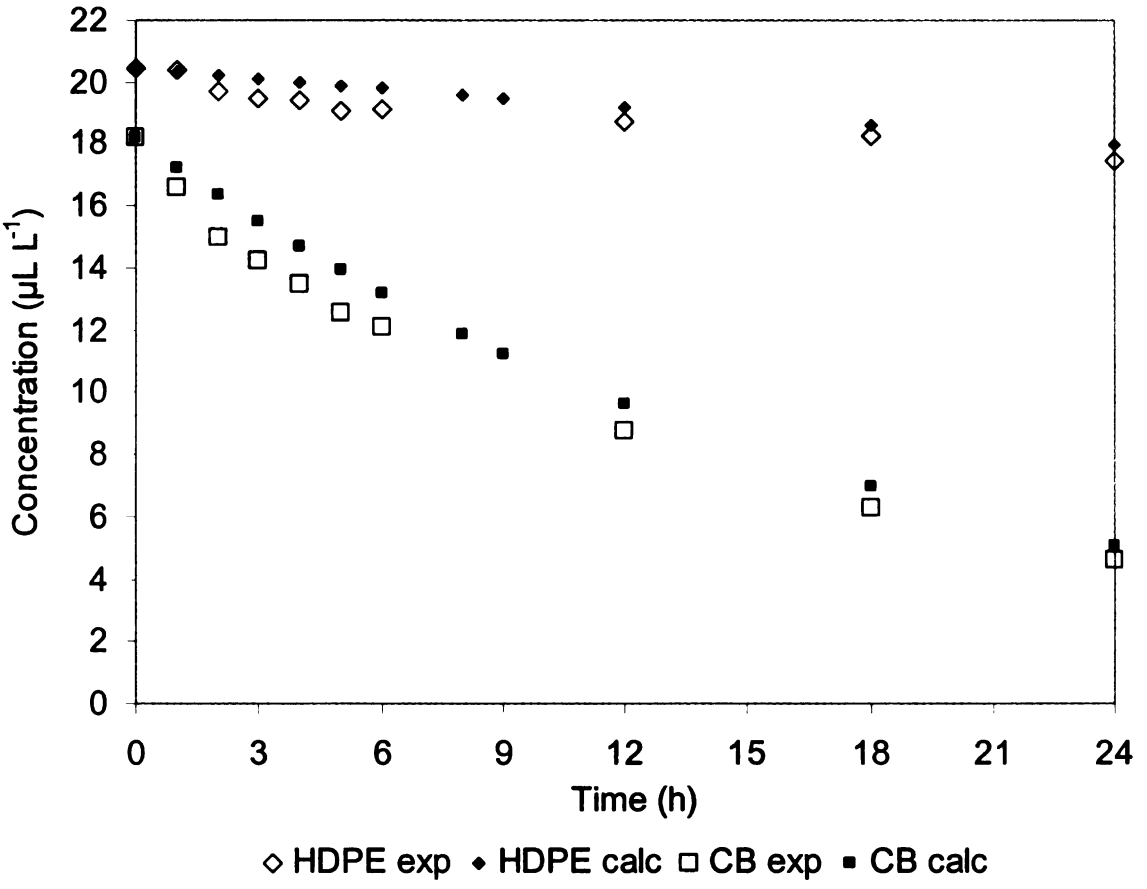


Figure C6. Comparison of experimental and estimated concentration of 1-MCP using the calculated k values (R = 8 kg/ $m^3$, Co = 20 µL $L^{-1}$, 80%RH at 20°C).

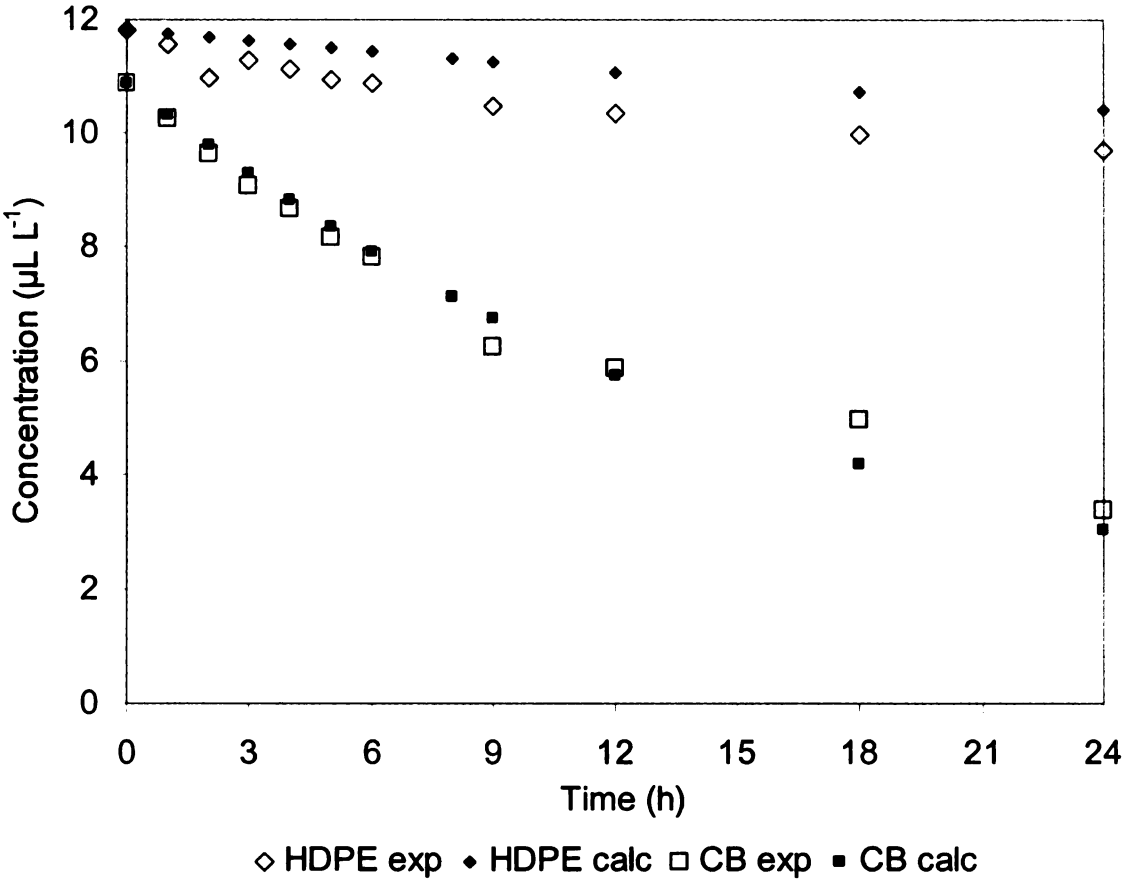


Figure C7. Comparison of experimental and estimated concentration of 1-MCP using the calculated k values (R = 4 kg/ $m^3$, Co = 10 µL $L^{-1}$, 80%RH at 20°C).

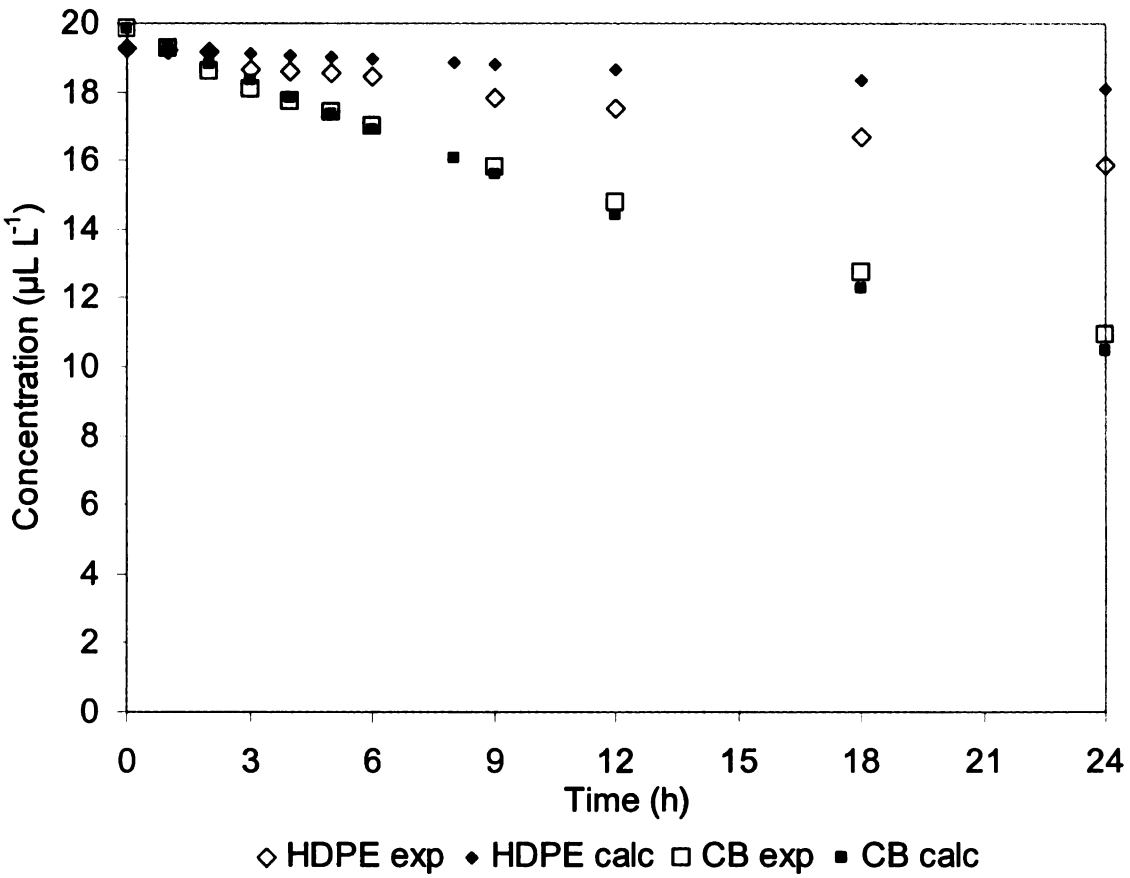


Figure C8. Comparison of experimental and estimated concentration of 1-MCP using the calculated k values (R = 4 kg/ $m^3$, Co = 20 µL $L^{-1}$, 80%RH at 20°C).

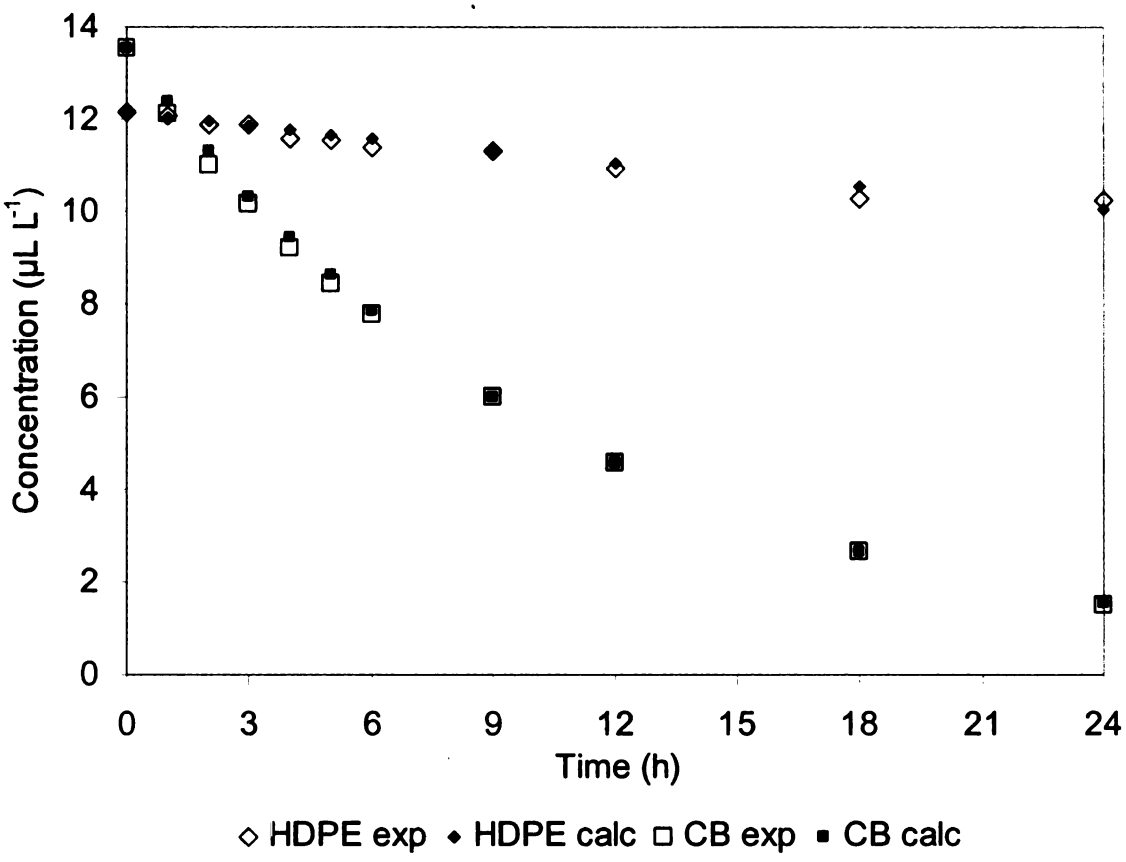


Figure C9. Comparison of experimental and estimated concentration of 1-MCP using the calculated k values (R = 8 kg/ $m^3$, Co = 10 µL $L^{-1}$, 95%RH at 20°C).

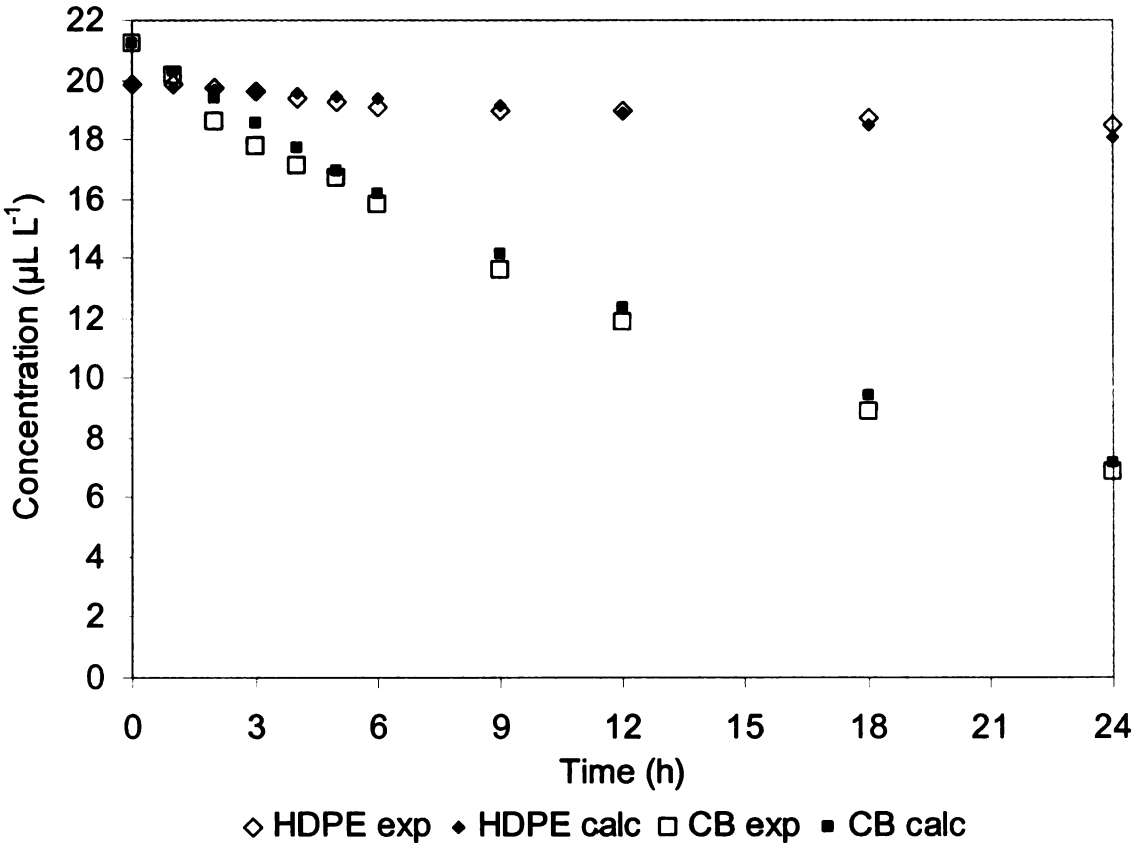


Figure C10. Comparison of experimental and estimated concentration of 1-MCP using the calculated k values (R = 8 kg/ $m^3$, Co = 20 µL $L^{-1}$, 95%RH at 20°C).

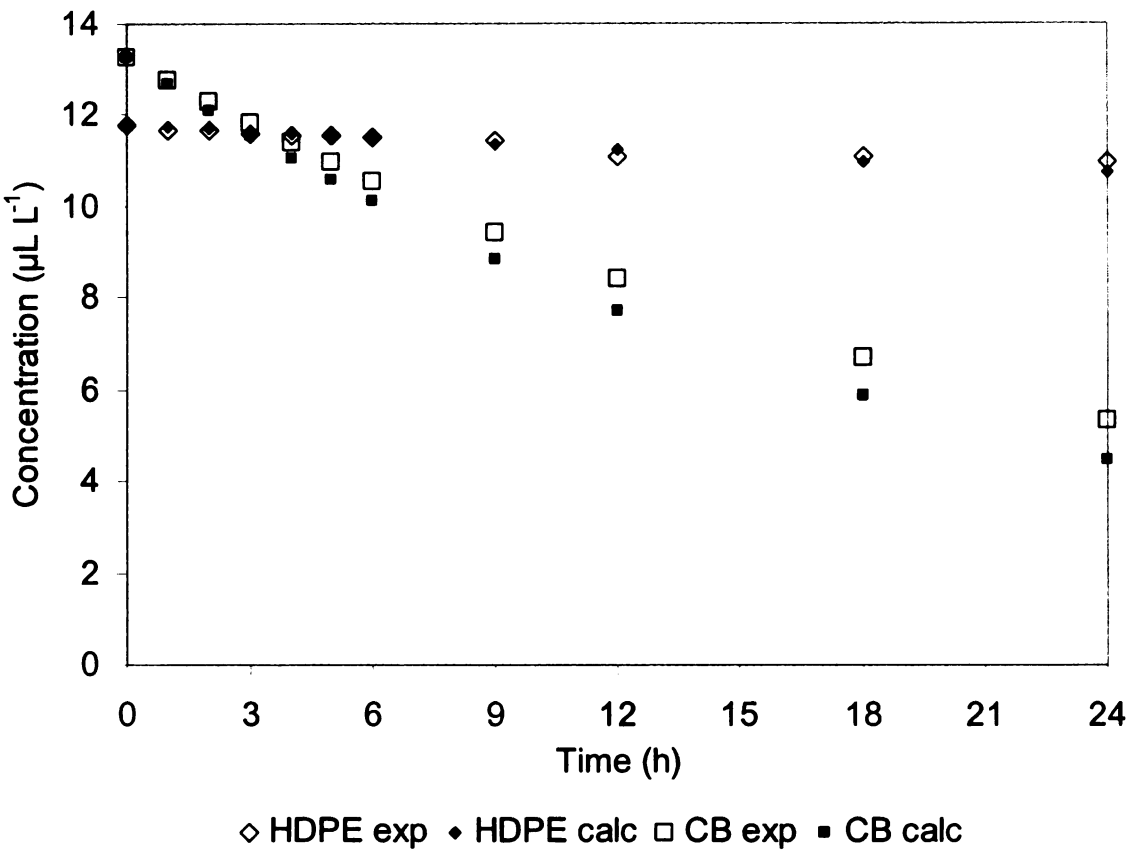


Figure C11. Comparison of experimental and estimated concentration of 1-MCP using the calculated k values (R = 4 kg/ $m^3$, Co = 10 µL $L^{-1}$, 95%RH at 20°C).

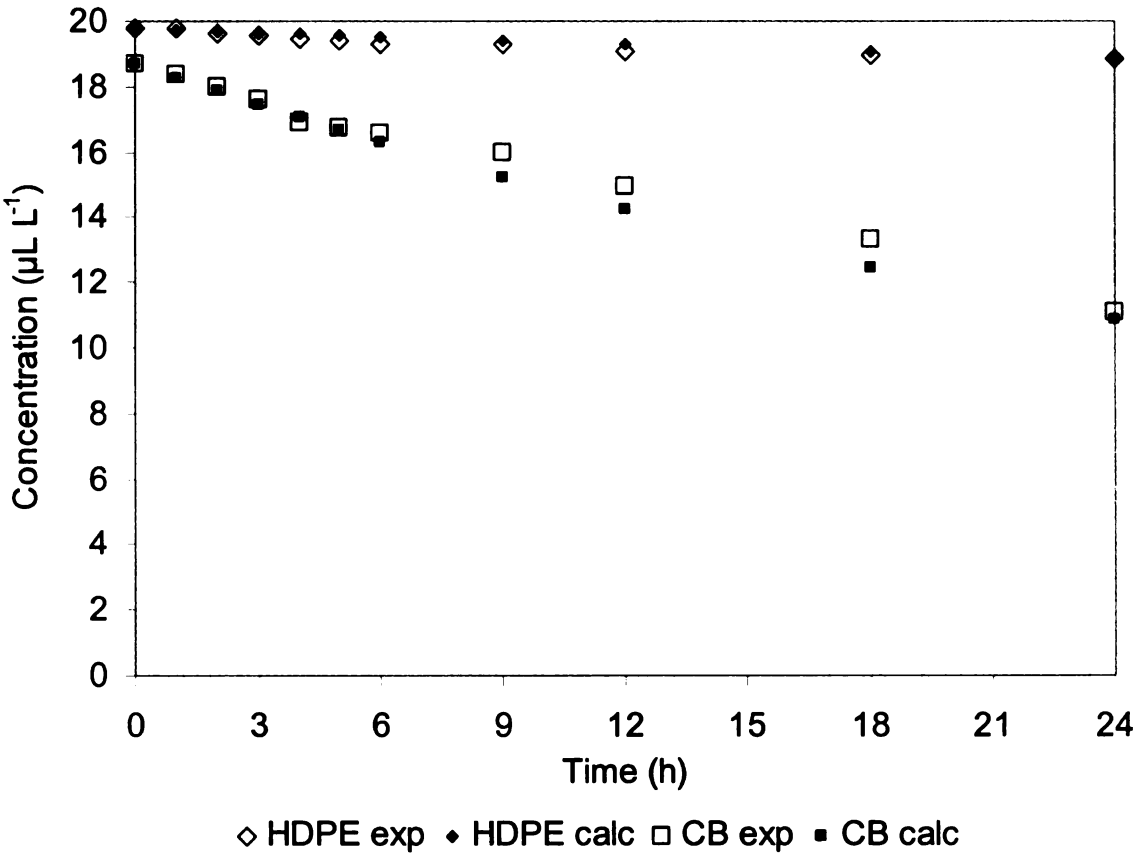


Figure C12. Comparison of experimental and estimated concentration of 1-MCP using the calculated k values (R = 4 kg/ $m^3$, Co = 20 µL $L^{-1}$, 95%RH at 20°C).