Release of 1-Methylcyclopropene from Heat-Pressed Polymer Films

J.H. Hotchkiss, C.B. Watkins, and D.G. Sanchez

ABSTRACT: Gaseous 1-methylcyclopropene (1-MCP) is an inhibitor of ethylene perception that is being used extensively for apples and ornamental products, and under intensive investigation for its potential benefits for other fruits and vegetables. 1-MCP is currently used in closed environments that maintain stable concentrations for several hours in order to be effective. However, food packaging materials that release 1-MCP at a predictable rate into the package headspace might be useful for application in inhibiting the deleterious effects of ethylene in the postharvest packaging and storage of some horticultural products. A 1-MCP/α-cyclodextrin (1-MCP–cd) complex was incorporated into several common packaging films by heat-pressing (dry-blend, lamination) and solution-casting methods. The release of 1-MCP from the films was quantified by gas chromatography with respect to time, loading of 1-MCP, temperature, relative humidity (RH), type of film, and film-forming method. Release of 1-MCP was rapid and high in films held at RH ≥ 75%. The rate of release was slow during the 1st 12 h and then increased during the next 24 to 36 h. Higher temperatures resulted in higher and faster release. A loading of 8 mg of 1-MCP–cd per 140 mg of polymer was found to be optimal. Pressing 1-MCP–cd containing films above 100 °C reduced the amount of 1-MCP remaining in the film. Incorporation into LDPE resulted in a higher and faster release than from PS, PVC, and PP polymers. 1-MCP release from a film matrix appears to be within the acceptable range for produce packaging applications.

Keywords: active, film, packaging, polymer, 1-methylcyclopropene (1-MCP)

Introduction

Ethylene is a plant growth regulator that affects many aspects of plant growth and development and from a postharvest perspective can have major effects on ripening and senescence (Saltveit 1999). These effects can be both positive and negative (Saltveit 1999), but typically control of ethylene production by technologies such as low temperature and modified atmospheres, as well as avoidance, ventilation, and chemical destruction of ethylene, is used by industry to maintain the quality of horticultural products (Watkins 2002). Recently, a new technology based on 1-methylcyclopropene (1-MCP), an inhibitor of ethylene binding (Sisler and Serek 2003), has been developed and approved for food use (EPA 2002). 1-MCP has been registered for use on a range of horticultural products, the fruit or vegetable being specific to each country (Watkins 2007). 1-MCP is already used extensively on apples and some ornamental products and is the subject of intense study around the world as a means of maintaining quality for fruits and vegetables (Blankenship and Dole 2003; Watkins 2006).

Commercial application of 1-MCP to horticultural products is based on release of gaseous 1-MCP from a 1-MCP/α-cyclodextrin complex in either powder or tablet form after addition of water or base solution. 1-MCP application is carried out in sealed rooms to ensure exposure of the crop to the chemical for several hours. Other strategies for 1-MCP application could include the combining of 1-MCP with an active packaging system. The patent literature (Kostansek 2002) suggests that low concentrations of cyclopropenes can be released from packaging materials that incorporate the cyclopropene. However, the use of 1-MCP in combination with modified atmospheres (MA) and/or packaging has been limited. The use of MA for prepackaging 1-MCP-treated bananas and mangoes has been reported (Jiang and others 1999; Jiang and Joyce 2000). Another possible use of 1-MCP in packaging could be for fresh-cut or minimally processed products as ethylene production is increased in many fresh-cut fruits and vegetables (Rolle and Chism 1987). Preventing accumulation of ethylene around fresh-cut products reduced the rate of softening in kiwifruits and bananas and of chlorophyll loss in spinach leaves, but not in broccoli (Abe and Watada 1991), but exacerbated chilling injury of tomato (Hong and Gross 2000). 1-MCP extended the storage life of fresh-cut lettuce (Wills and others 2002; Tay and Perera 2004), pineapple (Budu and Joyce 2003), and papaya (Ergun and others 2006), although 1-MCP does not always improve storability of fresh-cut products, for example, apple (Bai and others 2004) and banana (Vilas-Boas and Kader 2006). Where beneficial effects of 1-MCP have been obtained, these have sometimes been via its effects on maintaining better quality of the preprocessed product (Calderon-Lopez and others 2005; Ergun and others 2006). Lee and others (2006) have reported on the release of 1-MCP from package sachets but no data on the release from films are, to our knowledge, available.

Our objective was to investigate the release of 1-MCP from polymer films into which 1-MCP–cd complex had been incorporated. The 1-MCP–cd complex was incorporated into several common packaging films by heat-pressing (dry-blend) and solution-casting methods, and the release of 1-MCP from the films was quantified with respect to time, loading of 1-MCP, temperature, relative humidity (RH), type of film, and film forming method.

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Materials and Methods

Reagents (or active compound)

Technical grade SmartFresh™ containing 1-MCP/α-cyclodextrin complex (1-MCP–cd; 4.4% active ingredient) was obtained from

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AgroFresh Inc. (Rohm and Haas Co., Springhouse, Pa., U.S.A.). Technical grade consists of a 1:1 complex of 1-MCP in α-cyclodextrin (cd), uncomplexed cd, and approximately 6% to 8% water of crystallization. Gaseous 1-MCP is displaced from the cd by water, releasing it to the atmosphere. The SmartFresh powder was held under desiccation to prevent 1-MCP release until use. All polymer resins were purchased (Scientific Polymer Products Inc., Ontario, N.Y., U.S.A.) and were additive free.

Film formation

Cast films were obtained by mixing 10 mg 1-MCP–cd with 1 g of polymer resin which had been dissolved in an appropriate solvent. The mixture was poured onto a 15-cm glass plate and the solvent evaporated overnight in the dark at room temperature. After drying, the films were peeled off the plate, and stored until use as described below.

Heat-pressed films were prepared by thoroughly dry blending powdered polymer resins (LDPE, PVC, PP, PS, and EVOH) and technical grade (that is, SmartFresh) 1-MCP–cd (10 mg 1-MCP–cd powder [440 μg of 1-MCP] per gram of polymer) in powdered form, then heat pressing the dry blend between 2 sheets of Mylar set between the 2 preheated plates of a hot press (Model 341-20, Loomis Engineering & MFG. Co., Caldwell, N.J., U.S.A.). The temperature of the plates was stabilized at the desired pressing temperature (115 to 185 °C). The sheets were pressed and heated for 1 min at 210000 kPa. The films (approximately 102 μM of thickness) were peeled from the Mylar sheets and stored desiccated at ambient temperature until testing (1 to 2 d).

The release of 1-MCP from the compounded films was determined by placing the entire film sample in a 130-mL glass jar (Ball Corp., Muncie, Ind., U.S.A., product code 14400-80400) along with a metal clip to hold the film and a 2.0-mL vial containing the appropriate saturated salt solution (Wexler and Hasegawa 1954) or distilled water to provide the desired RH. The jars were sealed with metal lids fitted with rubber septa (Wheaton, Millville, N.J., U.S.A.) and further secured with silicone rubber sealant (General Electric Co., Waterford, N.Y., U.S.A.) which served as a sampling port. The amount of 1-MCP released from the film or 1-MCP–cd control over 120 h was determined by periodically analyzing the headspace in the jars for 1-MCP concentration. Headspace (0.5 mL) was withdrawn by gastight glass syringe (Model nr 81220, Hamilton Co., Reno, Nev., U.S.A.) and analyzed by gas chromatography with flame ionization detector (GC–FID). GC–FID conditions were Varian 6000 GC (Varian Inc., Walnut Creek, Calif., U.S.A.); CP-PoraPlot Q-HT fused silica capillary column 10 m × 0.53 mm with a 10-μm film;

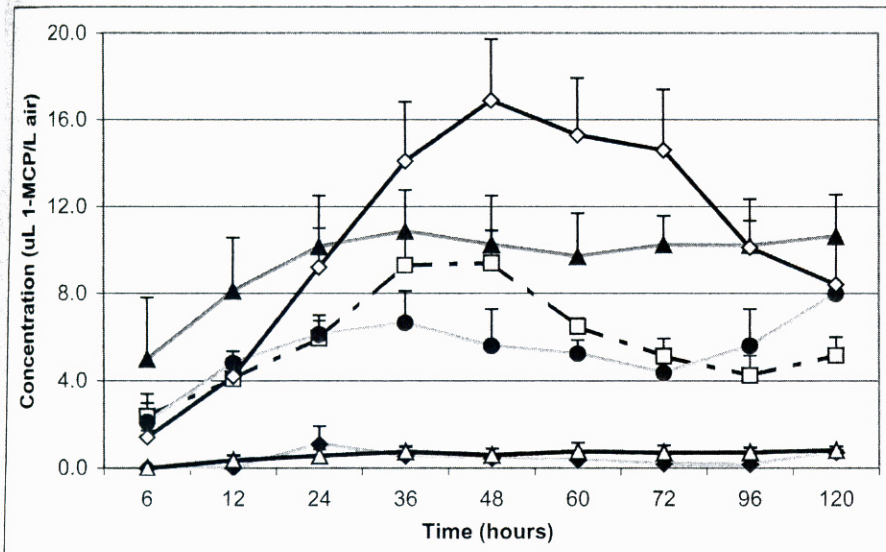

Figure 1—Headspace concentration of 1-MCP released from different polymer films containing 1-MCP–cd and pressed at different temperatures: LDPE, 115 °C (▲), PS 135 °C (□), PVC, 142 °C (●), PP, 165 °C (△), LDPE 185 °C (◇), and 1-MCP–cd control (◊). All films and the 1-MCP control were held at 22 °C and 100% RH. Vertical bars represent 1 standard deviation ($n = 3$).

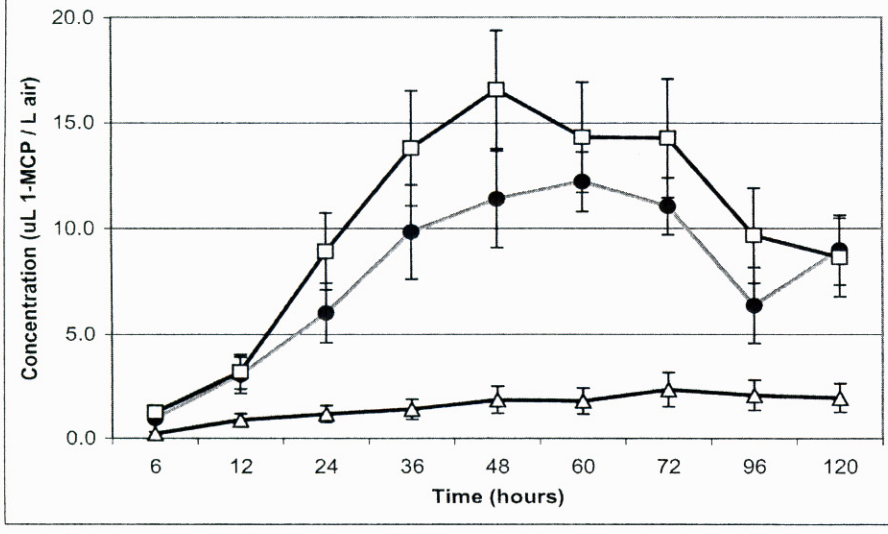

Figure 2—Headspace concentration of 1-MCP released from films containing 1-MCP–cd heat-pressed at 115 °C (●), 185 °C (△), 1-MCP control (□). All films and 1-MCP control were held at 22 °C and 100% RH. Vertical bars represent ± 1 standard deviation.

(Catalog nr 7558, Chrompack, The Netherlands) column temperature was 140 °C/min, increased to 200 °C at 30 °C/min, held at 200 °C for 3 min; carrier gas 2.5 mL/min N_2. 1-MCP concentration was determined against a 48.8-μL/L isobutylene in air external standard (Scott Specialty Gases, South Plainfield, N.J., U.S.A.). This assumes that the response factor for 1-MCP and isobutylene is unity. A Varian 4290 Integrator (Varian Inc., Walnut Creek, Calif., U.S.A.) was used to quantify the 1-MCP and isobutylene peaks. Three separate jars were used for each measurement.

Permeability measurements

A permeation apparatus as described by Al-Ati and others (2003) was used to determine the permeation rates for 1-MCP through LDPE films.

Statistical analysis

Minitab Release 14 (Minitab Inc., State College, Pa., U.S.A.) was used to test significance using the general linear model to determine the treatment and interaction effects and Tukey's test for comparing the levels. Three replicates per treatment and 10 slices per replicate were used in all experiments. Data were tested for multiple comparisons by analysis of variance (ANOVA) with least significant difference (LSD) between averages determined at the 5% level.

Results and Discussion

Only trace amounts of 1-MCP were released from any cast film. For example, the headspace concentration of 1-MCP released from cast PS and LDPE films reached 0.34 and 0.44 μL/L after 20 h, while the release of 1-MCP from 1-MCP–cd that had not been incorporated into film was 10 to 15 μL/L. We believe that 1-MCP was most likely lost during the solvent evaporation processes. This suggests that solvent casting may not be suitable for forming films that incorporate 1-MCP–cd. Therefore, all subsequent work was conducted with heat-pressed films.

The headspace concentrations of 1-MCP released from heat-pressed LDPE, PS, and PVC films were 10.8, 9.3, and 6.7 μL/L with maximum concentration being reached in 36 to 48 h (Figure 1). The control (1-MCP–cd alone) followed a similar time to maximum concentration but the absolute concentration was 17 μL/L. PP film pressed at 165 °C and LDPE film pressed at 185 °C film resulted in only trace 1-MCP concentrations (<1 μL/L). No detectable 1-MCP was released from heat-pressed EVOH films. These low release amounts were likely due to the high pressing temperature (185 °C), resulting in volatilization of the 1-MCP from the matrix. This is supported by the observation that LDPE films that were pressed at 185 °C had a much lower release than LDPE films pressed at 115 °C, suggesting that polymer processing temperature would have a large effect on the incorporation of 1-MCP in

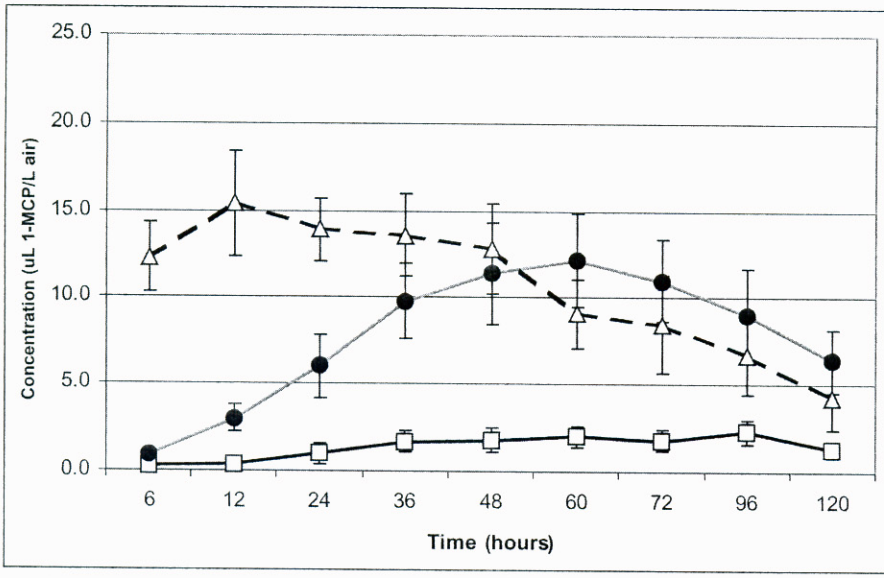

Figure 3—Headspace concentration of 1-MCP from heat-pressed LDPE films containing 1-MCP–cd and held at 56 °C (△), 22 °C (●), and 5 °C (□) for 6 to 120 h at 100% RH. Vertical bars represent ± 1 standard deviation ($n = 3$).

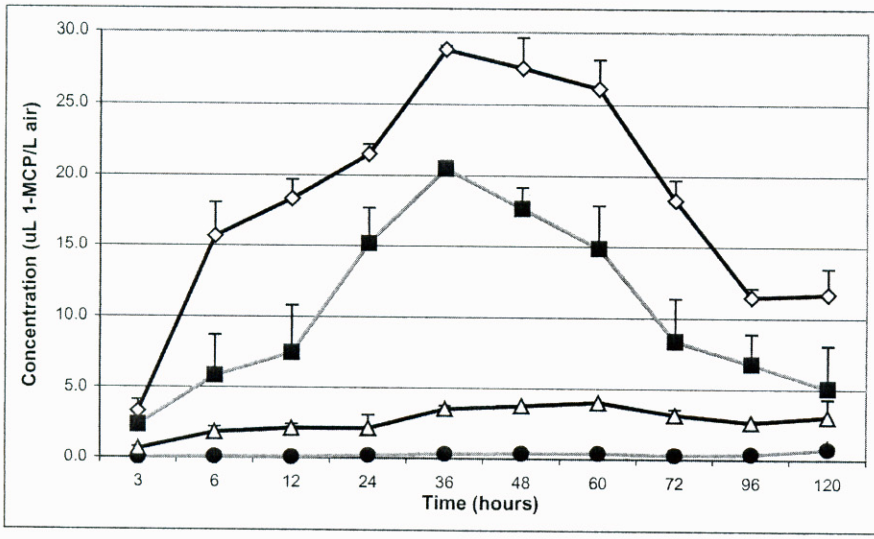

Figure 4—Headspace concentration of 1-MCP from 1-MCP–cd at 24 °C and 100% RH (◊), 75% (■), 52% RH (Δ), and 32% RH (●). Vertical bars represent 1 standard deviation.

polymer films (Figure 2). In all cases, including the controls, the concentration of 1-MCP in the jars decreased slightly after reaching a maximum. This was most likely due to absorption of the 1-MCP by the silicone rubber septum and/or the rubber sealing compound in the jar lids.

The optimum time and pressure for forming films incorporating 1-MCP–cd was 1 to 2 min at a pressure of 210000 kPa and a 5.5% loading 1-MCP–cd (w/w) and a heat press temperature of 115 °C, which is near the lower melt limit for LDPE (data not shown). This short-time and low-temperature process was thus used for further studies since it resulted in a higher release of 1-MCP. Adding 57 mg of 1-MCP–cd/g of LDPE (5.5% loading) was found to result in a suitable film with minimal loss of 1-MCP after a series of loadings were analyzed (1%, 3%, 10%, 15%, and 20%).

Increasing the temperature in which the jars containing films were held increased the rate of 1-MCP release from both free 1-MCP–cd and film containing 1-MCP–cd (Figure 3). Plotting the logarithm of headspace concentration against the reciprocal of temperature gave a straight line, which suggested that release followed Arrhenius behavior (not shown). The release from films was rapid and gave the highest concentration when held at 56 °C compared with lower temperatures. In contrast, 1-MCP-incorporated LDPE films held at 5 °C gave the lowest and slowest releases of 1-MCP (2.3 μL/L). In practice, this temperature release sensitivity should be taken into account.

When temperature was held constant and RH varied, the release of 1-MCP increased as the RH increased (Figure 4). At 36 h, 1-MCP release was 0.4 μL/L at 32% RH, 3.5 μL/L at 52% RH, 20.5 μL/L at 75% RH, and 28.8 μL/L at 100% RH, respectively.

The permeability of 1-MCP through LDPE at 100% RH resulted in a characteristic Fickian permeation and time lag curve (Figure 5). The permeability, solubility, and diffusivity coefficients for 1-MCP in LDPE were calculated as $D = 2.23 \times 10^{-9}$ cm^2/s, $S = 60.01$ cm^3 (STP)/(cm^3• atm), and $P = 13.4 \times 10^{-8}$ (cm^3 [STP]• cm)/(cm^2• atm• s). 1-MCP appears to readily pass through the polymer films tested. The diffusivity value of 1-MCP was lower than that of CO_2 and O_2 as was expected since 1-MCP is a larger molecule.

The above experiments were all conducted in vessels containing distilled water (that is, RH = 100%). In order to determine if cut fruits would provide sufficient moisture to cause release of 1-MCP, a 1.5 × 1.5 × 1.5 cm piece of fresh-cut apple was used in lieu of water to generate humidity within the container. The control for this experiment consisted of a similar sample of a 1-MCP-incorporated film that was placed inside the test system without any RH source. An additional control consisted of a 1-MCP–cd containing film and a 2-mL vial of distilled water to generate 100% RH. The humidity provided by the fresh-cut apple cube was sufficient to liberate the 1-MCP from the film (Figure 6). The release from the dry 1-MCP–cd was insignificant (data not plotted), while the release of 1-MCP from a 100% RH environment occurred at a faster rate than the apple

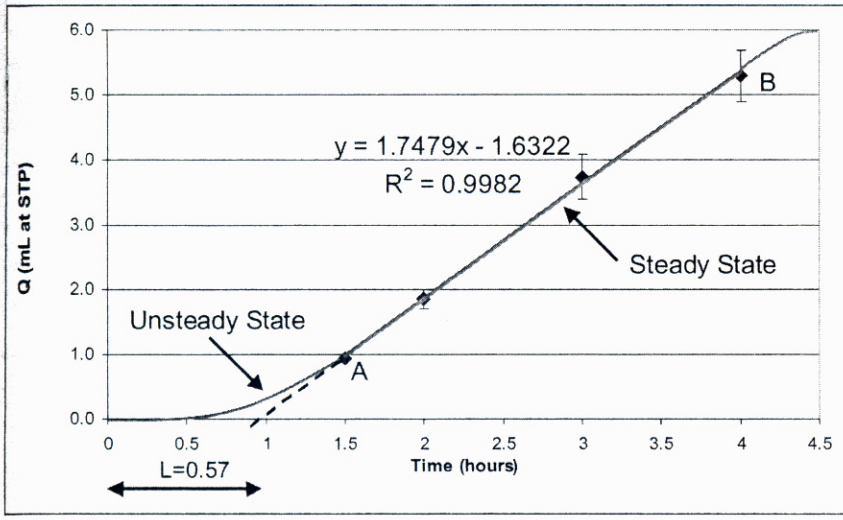

Figure 5—Permeation and time lag curve, where Q is the amount of penetrant (1-MCP), as a function of time for LDPE films. Extrapolation of the steady-state line AB to the time axis gives the time lag L as intercept, which along with the slope (Q/T) allowed us to calculate the permeability, solubility, and diffusivity values of 1-MCP in LDPE: $D = 2.23 \times 10^{-9}$ cm^2/s, $S = 60.01$ cm^3 (STP)/(cm^3• atm), and $P = 13.4 \times 10^{-8}$ (cm^3 (STP)• cm)/(cm^2• atm• s). Vertical bars represent ± 1 standard deviation.

$S = 1.53 \times 10^{-6}$ g/cm^3 • Pa

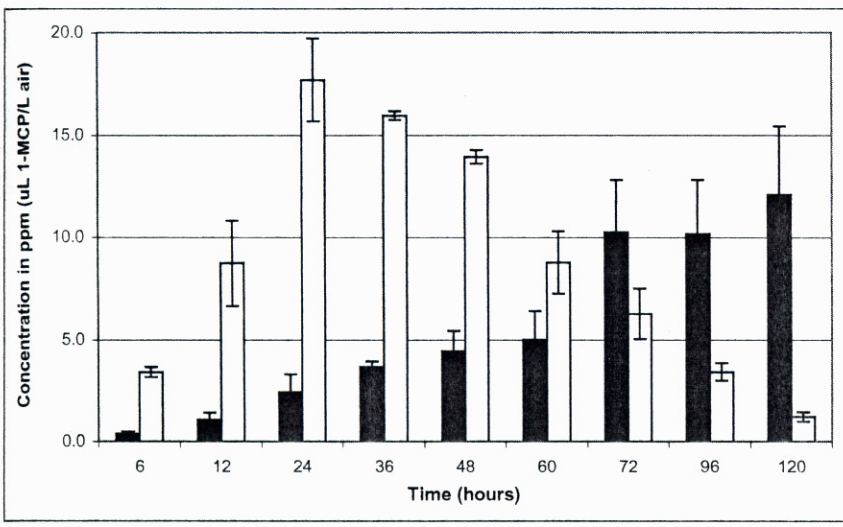

Figure 6—Headspace concentration of 1-MCP as a function of storage time: via moisture activated release of fresh-cut apple slices (■) compared with the 1-MCP–cd control (□). All films and 1-MCP–cd control were held at 22 °C. Vertical bars represent ± 1 standard deviation.

slice. These data indicate that 1-MCP was released from the LDPE film by the humidity originating from the apple piece. The apple tissue will absorb some of 1-MCP, which might be a factor in the final concentration achieved.

Conclusion

Polymer processing method and temperature strongly affected 1-MCP release, with low-temperature heat-pressed films having the highest release rates. The rate of release of 1-MCP, which occurred readily above 75% RH, was slow during the 1st 12 h but then increased during the next 24 to 36 h. A loading of 5.5% (8 mg of 1-MCP–cd per 140 mg of LDPE) was found to be the optimum for the creation of uniform polymer films. Higher holding temperatures result in a higher and faster release of the active compound. Taken as a whole, these results suggest that 1MCP–cd could be incorporated into a packaging film which would subsequently release 1-MCP during the storage of fresh-cut produce.

Additional work to control the release characteristics of 1-MCP from the packaging film is needed to further develop this concept. Evaluation of a broader range of films and layering structures should be undertaken. In addition, commercial application will require higher quality films and therefore refinement of the pressing process to optimize pressing time, loading, and temperature. Also, the effects of this concept on specific produce items will need to be studied. A multilayered structure in which the outer layer is a high barrier to 1-MCP could be used to prevent loss to the general environment. This work also indicates that loss of 1-MCP during film storage could be prevented by ensuring that the films are held in low-humidity environments or packaged in high barrier films until use.

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