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Evaluation of Pheromone Release from Commercial Mating Disruption Dispensers

ELIZABETH TOMASZEWSKA,[†] VINCENT R. HEBERT,*[,†] JAY F. BRUNNER,[‡] VINCENT P. JONES,[‡] MIKE DOERR,[‡] AND RICHARD HILTON[§]

Food and Environmental Quality Laboratory, Washington State University, 2710 University Drive, Richland, Washington 99354, Tree Fruit Research Extension Center, Washington State University, 1100 North Western Avenue, Wenatchee, Washington 98801, and Southern Oregon Research and Extension Center, Oregon State University, 569 Hanley Road, Medford, Oregon 97502

Pome fruit growers and crop consultants have expressed concerns about the seasonal release performance of commercial codling moth mating disruption dispenser products. Because of these concerns, we developed a laboratory flow-through volatile collection system (VCS) for measuring the volatile release of the codling moth sex pheromone, codlemone, from commercially available hand-applied dispensers. Under controlled air-flow and temperature conditions, the released vapor was trapped onto a polyurethane foam adsorbent followed by solvent extraction, solvent reduction, and GC/MS determination. Method recovery and breakthrough validations were performed to demonstrate system reliability before determining codlemone release from commercial dispensers field-aged over 140 days. The volatile collection was carried out in a consistent manner among five dispenser types most commonly used by growers, so that direct comparison of performance could be made. The comparison showed differences in the amount of pheromone released and in the patterns of release throughout the season between dispenser types. The variation in release performance demonstrates the need for routine evaluation of commercially marketed mating disruption dispensers. We believe that the simple and cost-effective volatile collection system can assist pheromone dispenser manufacturers in determining seasonal dispenser performance before new products are introduced into the commercial market and in rapidly verifying dispenser release when field-aged dispenser efficacy is in question.

INTRODUCTION

The codling moth (*Cydia pomonella* L., CM) is a major insect pest of pome fruit (*1*) that has been traditionally controlled by organophosphorus (OP) insecticides sprayed 2−4 times per growing season. However, recent mandatory re-evaluation of pesticide tolerances under the Food Quality Protection Act of 1996 has resulted in the elimination or label use restriction for OP insecticides commonly used for CM control. Furthermore, the development of CM resistance to OP insecticides has also contributed to the uncertainty over the future utility of this class of insecticides (*2*, *3*).

In response to the potential problems associated with OP use, pome fruit growers in the Pacific Northwest and California have adopted the use of the sex pheromone, codlemone [(*E*,*E*)-8,-10-dodecadien-1-ol], to control the CM population (*4*−*6*). Although the sex pheromone of codling moth is composed of at least five compounds, codlemone is considered to be the most important component (behaviorally) of the blend produced by the female CM. When a sufficient amount of codlemone is intentionally applied to the orchard air, the ability of the male CM to locate females is reduced, thus preventing or delaying mating, and is typically referred to as mating disruption (MD). The use of pheromones to suppress CM mating can significantly reduce the population of the pest below levels that cause economic harm to apple and pear growers (*5*). Because of the documented success of mating disruption, this technology has become a very important part of the management for CM in the Pacific Northwest. In addition, because of its very low human toxicity and high target specificity, in the August 30, 1995 *Federal Register* (volume 60, number 168), the Environmental Protection Agency (EPA) classified codlemone as a reduced risk pesticide and has granted its registration exempt from food and feed tolerances.

Unlike insecticides that are designed to kill on contact or by ingestion following a single application, pheromone delivery systems must provide a constant release of adequate levels of pheromone throughout the growing season while adult moths are present. In the Pacific Northwest, the most commonly used

* To whom correspondence should be addressed. E-mail: vhebert@tricity.wsu.edu.
[†] Food and Environmental Quality Laboratory, Washington State University.
[‡] Tree Fruit Research Extension Center, Washington State University.
[§] Southern Oregon Research and Extension Center, Oregon State University.

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delivery systems are solid matrix dispensers designed to release codlemone at a continuous rate for 140−160 days. The dispensers are applied by hand in the tree canopy at rates of 200−400 per acre depending on the product. Currently, there are four major CM solid matrix manufacturers each making dispensers with a slightly different structure and release rate characteristics.

Several measurement methods have been employed to ensure that the dispenser type is adequately releasing pheromone over the season. These methods include (1) gravimetric (i.e., weighing/notating percent loss from the field-aged dispensers at timed intervals) (*7*−*9*), (2) total organic solvent extractions of dispensers to determine residual pheromone concentrations after field aging (*10*−*12*), or (3) flow-through nondestructive collection of the pheromone vapor (*13*−*15*).

Gravimetric methods that weigh dispensers at specified days over the season lack precision and sufficient accuracy to establish pheromone release profiles for all of the different types of dispensers (*16*). However, solvent extractions of the residual pheromone from field-aged dispensers are more precise in estimating product release. The key to making the extraction method feasible is that the organic solvent must efficiently dissolve all of the pheromone from the solid matrix dispenser. This solvent extraction method has the advantage of quantifying residual pheromone and possible degradation products by gas chromatography (GC) and allows calculation of the release rate over a given time interval. However, care must be exercised because it is assumed that the difference between the initial time zero concentration and that of the aged dispenser is equal to codlemone released. There exists the possibility that nonvolatile degradation products formed within the dispenser could not be captured by the GC. Flow-through dynamic collection may provide a more precise measurement technique for pheromone release from the field-aged dispensers. An important assumption of this approach is that every dispenser type should be subjected to similar air-flow characteristics at constant atmospheric pressure and temperature conditions to ensure consistent and comparable pheromone release rate information. Unfortunately, solid matrix dispensers are not uniform in their sizes and shapes, factors that could influence air-flow characteristics. Regardless of the physical characteristics of the dispenser, an ideal apparatus for measuring pheromone release rates should allow for quantitative vapor recovery while minimizing decomposition of the released compounds.

Dynamic gas flow-through systems have previously been used to collect pheromone vapors using an array of different adsorbents that include C18 (*17*−*19*), silica (20, *21*), Super-Q (*22*), Tenax (*13*, *23*), Porapak-Q (*24*−*26*), and activated charcoal (*27*). The above methods rely on trapping the gas-phase constituents onto the adsorbent bed followed by solvent extraction and analysis of the concentrated solvent extract either by sampling the headspace or solvent by GC. GC methods have also been developed that rely on purge and trap vapor enrichment followed by thermal desorption (*13*, *27*). Many of these collection methods were developed to qualitatively capture and characterize complex blends of insects' pheromones. Because methods were not developed to be quantitative, adsorbent collection efficiency and stability evaluations during collection were not normally performed. Moreover, many of the above volatile capture methods are too complex for rapid analysis of the large numbers of samples required to quantitatively evaluate pheromone release behavior in the orchard environment.

Pheromone mating disruption has been shown to be a proven tool for controlling CM populations on a region-wide basis (*4*−*6*). Although dispenser design and release performance has continually improved, CM damage can periodically be widespread and dispenser release performance may come into question. Growers and manufacturers often demand rapid information on dispenser release performance to take the necessary corrective action(s).

To respond to the needs of growers, crop consultants, and dispenser manufacturers, we developed a volatile collection system (VCS) to rapidly evaluate dispenser release behavior. Our overarching objectives were to (1) directly assess pheromone release in a consistent manner from individual field-aged dispensers from different manufacturers, (2) determine individual dispenser release rates quickly (i.e., in hours not days), and (3) provide a tool for growers to quickly verify field-aged dispenser release when product efficacy comes into question. Herein, we present system verification and dispenser release evaluations of five commercially marketed products that were field-aged over a 140-day orchard-growing season.

MATERIALS AND METHODS

Chemicals, Reagents, and Materials. A codlemone [(*E*,*E*)-8,10-dodecadien-1-ol] standard was acquired from Shin-Etsu (Tokyo, Japan). The myristic acid methyl ester (MAME) system testing surrogate standard was obtained from Sigma (St. Louis, MO). The following chemicals were used throughout the study: HPLC-grade hexane, ethyl acetate, acetone, and methanol (J. T. Baker; Phillipsburg, NJ). The extraction solvent (90% hexane/10% ethyl acetate) was prepared daily prior to analysis. Adsorbent polyurethane foam PUF cartridges and their glass holders were obtained from Supelco (Bellefonte, PA). All customized Teflon components for the volatile trapping system were obtained from Savillex Inc. (Minnetonka, MN).

VCS. To assay the individual field-aged dispensers in a consistent and reproducible manner, we selected a pressurized air delivery source that provided constant air flow to the five-chamber VCS collection assembly (parts **A** and **B** of **Figure 1**). All tubing, connections, and ferrules leading to each 1000-mL collection chamber and to the glass PUF holder were constructed of Teflon to minimize gas-phase wall adsorption. For each volatile collection, a single dispenser together with a known amount of the MAME surrogate applied to a small piece of glass microfiber filter paper (934-AH, Whatman) was suspended in the center of the collection chamber using Teflon tape. Accounting for material balance of the surrogate provided a means to determine system reliability/performance on a dispenser/dispenser basis.

After placing the dispenser and MAME surrogate in the collection chamber and connecting all system components, the air flow was started and run at ambient room temperature (20 ± 2 °C) for 2 h at a rate of 10 L/min for each sampling chamber. Flow rates and humidity of the air leaving the collection chamber during the sampling period were routinely monitored and recorded. A Hobo temperature device was placed in one of the five collection chambers for monitoring air temperature over the 2-h collection time frame. Temperature information was recorded every 5 min throughout the collection period. After the collection interval, the air flow was stopped; the PUF cartridge was removed from the system and placed into a 100-mL glass extraction jar together with the surrogate-fortified filter paper. All surfaces of the apparatus in contact with volatiles were rinsed with the extraction solvent (10% ethyl acetate/90% hexane) and transferred to the same extraction jar. Afterward, the extraction jar was filled with extraction solvent to the point of PUF saturation. The PUF/filter paper sample was then ultrasonicated for 10 min followed by suction filtration. The suction-filtered PUF/filter-paper sample was returned to the jar and resaturated with the extraction solvent and then ultrasonicated. The two solvent extracts were combined and evaporated to near dryness (approximately 2 mL) by rotary evaporation at 30 °C under vacuum. The concentrated solvent extract was then transferred to a 15-mL centrifuge tube with a sufficient amount of hexane and brought up to a final volume suitable for analysis. With each set of samples (four replicate dispensers) a control blank PUF was also extracted and analyzed.

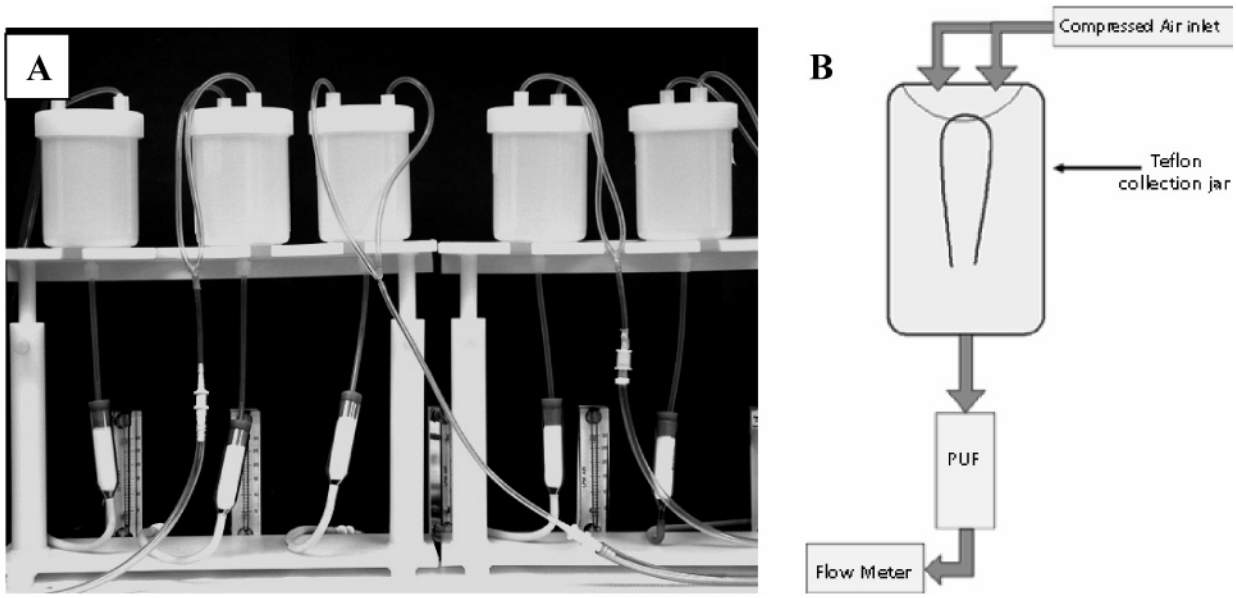

Figure 1. (A) VCS five-chamber system. (B) Individual system components.

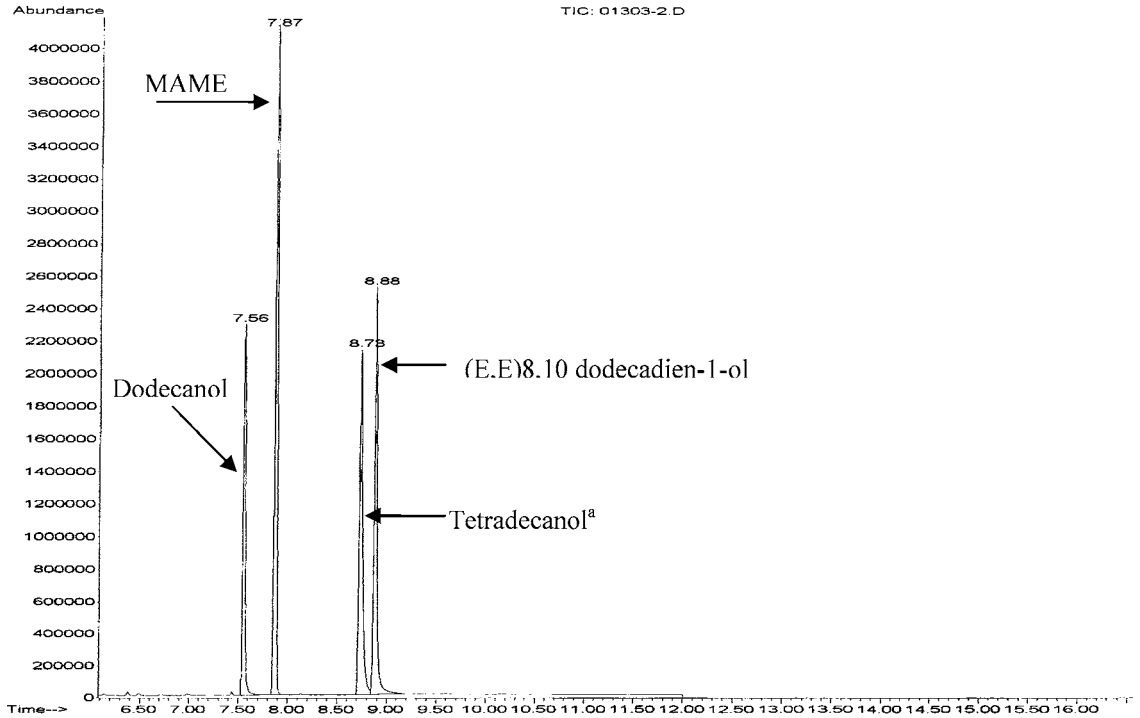

Figure 2. Total ion chromatogram of pheromone standard, with a 4 μg/mL concentration. Dodecanol and tetradecanol are present in the standard solution beside codlemone for evaluation of certain dispenser types that contain a pheromone blend consisting of these three substances.

An Agilent 6890N gas chromatograph with 5973N mass selective detection (MSD) was used for pheromone quantification. The MSD was run in total ion chromatography mode (TIC) scanning from 50 to 300 *m*/*z*. A fused silica EC-Wax capillary column 30-m long and 0.25-mm inside diameter with 0.25-μm film thickness (Alltech) was used to resolve codlemone and MAME. The carrier gas was ultrapure helium at a flow rate of 1 mL/min. The pulsed splitless injector temperature was set at 200 °C. The GC/MS interface temperature was 280 °C. The quantity of codlemone and MAME in the samples was calculated based on external standards using multilevel calibration and linear regression. **Figures 2** and **3**, respectively, show total ion chromatograms for a codlemone-mixed reference standard and chromatography from an individual VCS field-aged dispenser evaluation.

VCS Performance Evaluations. *Method Recovery*. To verify that solvent extraction efficiencies were quantitative, fortification samples were prepared by injecting known concentrations of codlemone (in hexane) directly onto the PUF at three different fortification levels (10, 50, and 100 μg) in triplicate. MAME was fortified on the PUF and filter paper at similar solution concentrations for recovery evaluation. The PUF adsorbent cartridges and MAME filter papers were extracted according to the above procedures.

Breakthrough Testing. To verify that codlemone and MAME remained sorbed to the PUF over the experimental time frame, PUF assemblies were fortified with 50 μg of codlemone and MAME (each in hexane) and attached to the VCS. Air was passed through the chamber at 10 L/min for 2 h to simulate actual gas-phase sampling conditions. Afterward, the PUF cartridge was removed and extracted according to the above procedures. The breakthrough experiment was replicated 3 times.

Vapor Recovery. A series of vapor collection experiments were carried out to establish the efficiency of the apparatus for collecting gas-phase pheromone/surrogate on the PUF adsorbent. The bottom inner

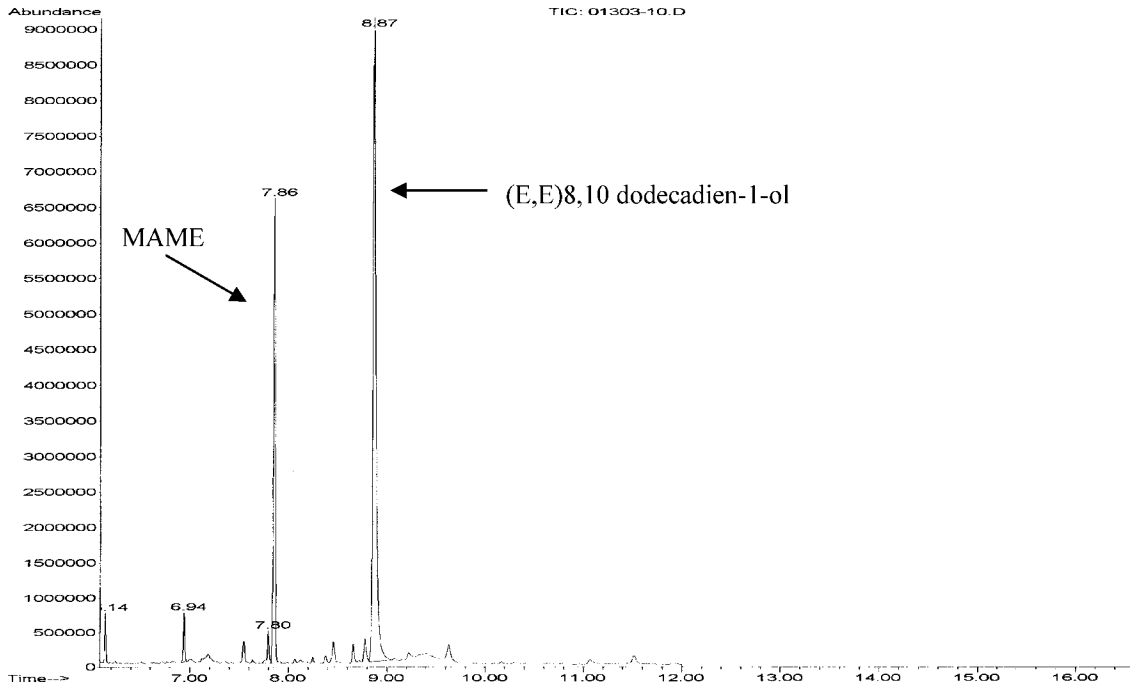

Figure 3. Total ion chromatogram of VCS field-aged analyzed SP-1 dispenser sample.

surface of each collection chamber was fortified with 10, 50, and 100 μg of codlemone and MAME in hexane and then closed. To raise the volatility of the compounds, the bottom of the collection chamber was slightly warmed using heat tape. The air was passed through the apparatus for 2 h at a flow rate of 10 L/min. After 2 h, the flow was stopped and the collection chamber, lid, and tubing were rinsed with the extraction solvent. The PUF cartridges and chamber rinse were analyzed separately as previously described. The amount of pheromone extracted from PUF and the amount remaining in the system were added together for a total material balance. This procedure was repeated 3 times for each codlemone and MAME concentration.

Performance Evaluation of Solid Matrix Dispensers. Dispensers for analysis were provided by their manufacturers and included two types of polyethylene tube twist tie dispensers (PET-1 and PET-2), two types of membrane dispensers (MB-1 and MB-2), and a spiral polymer dispenser (SP-1). Dispensers PET-2, MB-1, and MB-2 applied in the orchard in the rate of 200 per acre are loaded with approximately 215, 270, and 160 mg of codlemone, respectively. PET-1 and SP-1 dispensers loaded with half of that amount (99 and 117 mg, respectively) are applied in the orchard at a double rate of 400 dispensers per acre. The dispensers were aged to 140 days at orchard locations in Wenatchee, WA, and Medford, OR, during the 2003 growing season. At 14-day intervals, dispensers of each type from each location were collected and delivered to the Food and Environmental Quality Laboratory (FEQL) at Washington State University for VCS determination. After arrival, all dispensers were stored at ca. −15 °C. Approximately 24 h before volatile collection, the dispensers were allowed to equilibrate at room temperature. The temperature and air flow were monitored closely during VCS sampling. Any acquired data sets outside the range of specified temperature (20 ± 2 °C) and airflow rates (10 ± 1 L/min) were rejected, and sample collection was repeated. Cylinder air humidity was routinely measured. The volatilized pheromone collected over the 2-h air-sampling period was corrected to obtain release estimates over a 24-h time interval (i.e., mg/day).

RESULTS AND DISCUSSION

VCS Performance Evaluations. To provide accurate and reliable assessments of pheromone release, we designed the VCS with the following criteria in mind: (1) each individual dispenser type must be subjected to similar air-flow and temperature conditions, (2) pheromone(s) evaporating from the dispenser surface must be quantitatively collected on the adsorbent bed, and (3) solvent extraction of pheromone from the adsorbent must be consistent and reproducible.

The use of positive air pressure allowed us to maintain a stable air flow through each VCS chamber while minimizing the potential for system contamination from laboratory ambient air. Although various investigators have used nitrogen as a carrier gas to prevent the oxidation of pheromone compounds (*15*, *18*, *20*, *21*, *24*), we chose to use air because of its environmental relevance. Our preliminary evaluations indicated that codlemone fortified on PUF was not appreciably oxidized or isomerized over the 2-h experimental sampling time frame using air as a carrier gas. We found that PUF, when compared to other adsorbents, had the distinct advantage of high adsorptive capacity with very low air resistance and thus allowed 10 L/min air flows without measurable breakthrough or backpressure. Using a clean air source and ultrapure solvents also allowed us to collect and extract codlemone from the PUF without additional sample cleanup. In an earlier study, van der Kraan and Ebbers (*28*) also found PUF as an effective adsorbent for isolating the semivolatile lepidopterian insect pheromone, tetradecen-1-yl acetate, from air.

Pheromone sorption to the surfaces of glass walls has been reported to be problematic, even after taking precautions such as silanization (*13*). Our use of Teflon chambers and Teflon connections effectively minimized surface adsorption. In our VCS recovery evaluations, we did not collect more than 4% of the fortified codlemone and MAME materials from surface solvent washes of all system components. In addition to its inert surface, the individual Teflon chamber system components were easy to clean with the organic solvent and could be oven-dried at high temperature. Because of our space limitations, the VCS contained five Teflon chambers. The design, however, could accommodate many more dispenser chambers while maintaining constant air flow through each chamber.

Our preliminary VCS evaluations indicated that the system could reliably and reproducibly quantify pheromone released from individual commercial dispensers within a 2-h air-sampling period. Codlemone and MAME were recovered from fortified PUF with average efficiencies of 104 (±12) and 104% (±8%),

respectively. Residual MAME was extracted from filter papers with an average efficiency of 104% (±1%). In replicated breakthrough evaluations, we recovered 99% (±5%) codlemone and 101% (±2%) MAME from the surface-fortified PUF adsorbent cartridges. Moreover, the vapor collection efficiency for codlemone and MAME was 92 (±7) and 96% (±7%), respectively. The GC/MS in total ion-monitoring mode provided sufficient analyte sensitivity to restrict the time needed for air sampling to 2 h. Total ion mode also allowed monitoring for possible isomerized or oxidative products. However, we did not observe any appreciable gas-phase pheromone degradation products emitted by the field-aged dispensers over the experimental time frame.

In the early stages of developing the pheromone extraction method, we encountered problems with periodic low recoveries of codlemone (e.g., 60−70%). These recovery losses, as we later discovered, were attributed to high evaporative losses during rotary evaporation and also from excessive "stickiness" of codlemone to laboratory glass surfaces during transfers. Slower evaporation, with temperatures not higher than 30 °C, during the solvent concentration step, and very careful and thorough solvent rinsing of all laboratory glass surfaces was required for maintaining accurate and reproducible codlemone recoveries.

VCS Evaluation of Field-Aged Dispensers. Our main objectives were to (1) comparatively assess pheromone release from five field-aged dispenser types of different sizes and shapes, (2) verify that field-aged dispenser types were continually releasing codlemone regardless of field aging, and (3) assay if dispenser release is similar at different geographical locations in the Pacific Northwest. We analyzed 475 individual field-aged dispensers collected at 14-day intervals in Oregon and Washington in 2003. The average surrogate MAME recovery from the total number of individual dispensers was 97 ± 6%.

Parts **A**−**C** of **Figure 4** and parts **A** and **B** of **Figure 5** present graphic results of adjusted codlemone release rates (in mg/day) averaged for four replications of each dispenser type at each interval date at both Washington and Oregon orchard locations. We observed that all five types of dispensers were still releasing codlemone after 140 days of aging in both orchards. A constant near zero-order rate of release was not evident for any of the field-aged dispenser types. Pseudo-first-order pheromone vapor releases were more closely approximated for the PET-1, PET-2 (parts **A** and **B** of **Figure 4**), and MB-2 (**Figure 4C**) dispenser types. Similar release behaviors were observed for these three dispenser types over the 140-day field-aging period at the two orchard locations. Continuous but seasonally and individually variable dispenser release more appropriately described the behavior of MB-1 and SP-1 dispensers (parts **A** and **B** of **Figure 5**). In addition, their behavior at different orchard locations varied sporadically, particularly for dispenser MB-1.

PET-1 dispenser released codlemone in the range from 2.5 to 2.8 mg/day over the first 14 days of field aging. Release gradually decreased to 1.1−1.8 mg/day over the next 28 days and leveled off at ca. 0.8 mg/day through ca. 100 days. Afterward, there was a noticeable attenuation in the release rate to approximately 0.5 mg/day over the remainder of the 140-day study (**Figure 4A**). For PET-2 dispensers, the pattern of release was similar to that of PET-1 dispensers but the release rate was slightly greater over the entire 140-day period. This dispenser type started releasing approximately 3.5 mg of codlemone per day but steadily attenuated toward the end of the season with an average but steady release rate of 0.5 mg/day (**Figure 4B**). The small differences in release among these

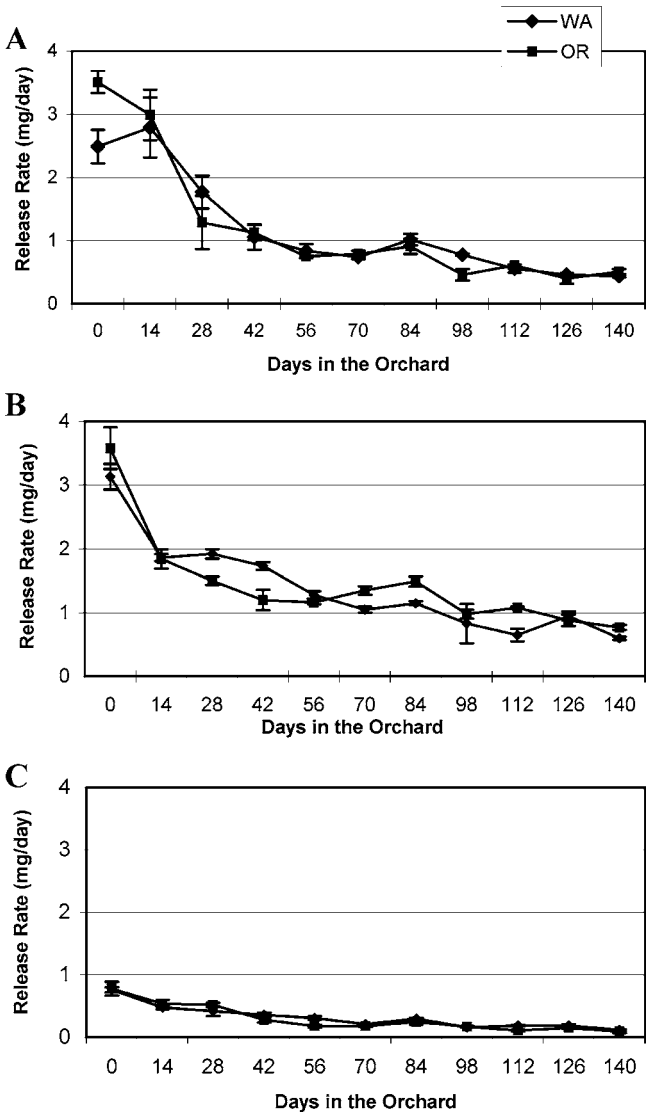

Figure 4. Field-aged release rates of codlemone from (A) PET-1, (B) PET-2, and (C) MB-2 mating disruption dispensers.

similarly designed dispensers was surprising because the PET-2 is loaded with 2 times more codlemone. The greater rate of chemical release during the first 14 days for both PET dispensers can be attributed to the fact that these dispensers are charged or conditioned to have codlemone at the dispenser surface, thus aiding in rapid release during the first critical few weeks of the moth-mating season (personal communication, Dr. Don Thomson, DLS Consulting Services). After this initial loss, codlemone release more closely approximates pseudo-first-order release rates throughout the moth-mating season. This near first-order depletion was also observed for MB-2 dispensers. However, for this dispenser type, the release rate is substantially less than the comparably loaded PET-2 dispenser. The 0-day release rate of 0.76 mg/day slowed considerably to 0.4 mg/day after 14 days of field aging. This dispenser showed a very low codlemone release rate at day 70 and beyond (0.16 mg/day, **Figure 4C**).

The release behavior of SP-1 and MB-1 dispensers contrasted sharply to the PET and MB-2 dispenser types. Although there was no clear pattern in release behavior, MB-1 dispensers released relatively high amounts of codlemone throughout the moth-mating season with maximum release rates of 2.7 mg/day at day 56 in Wenatchee, WA and 2.4 mg/day on day 112 in Medford, OR (**Figure 5A**). The measurements of release rates were highly variable for this dispenser at a given collection date,

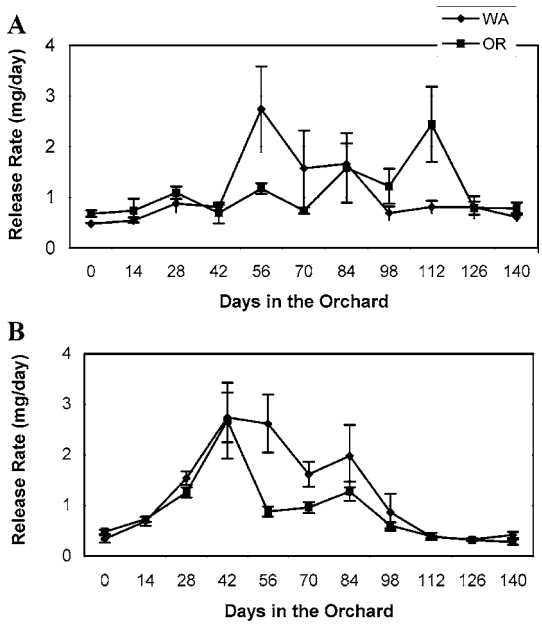

Figure 5. Field-aged release rates of codlemone from (**A**) MB-1 and (**B**) SP-1 mating disruption dispensers.

particularly as the dispensers aged in the field. For SP-1 dispensers codlemone release rate (0.3−0.7 mg/day) was slow over the first 14 days. The release rate increased with dispenser age, attaining maximum rates in midseason. After day 84, the codlemone release rate from SP-1 dispensers steadily declined to approximately 0.4 mg/day (**Figure 5B**).

In summary, we observed that all of the tested dispenser types were still releasing codlemone after 140 days of aging in the orchard at both locations. It is not certain whether the amounts of codlemone released from some of the dispenser types at the end of the season were sufficient to control the 2nd CM generation. We also observed differences from dispenser-to-dispenser type in the amount of total codlemone released throughout the season, with the highest being PET-2 and the lowest being MB-2. There were also major differences in release kinetics among dispenser types. None of the dispenser types meets the desired goal of a constant near zero-order rate of release. PET-1, PET-2, and MB-2 codlemone losses more closely approximated dose-dependent pseudo-first-order release. In the case of the other two dispenser types, MB-1 and SP-1, the release profile showed a continuous but seasonally variable codlemone release. In addition, individual dispenser release rates on some sample dates for these last two dispenser types were highly variable, with standard deviations in the range of 50−90%. We eliminated the system problems as a cause of these highly erratic release rates by monitoring the recovery values of our surrogate, which fell between 85 and 111%. Additionally, if the cause of this high variability was faulty instrumentation, it would have affected equally all of the dispenser types and not just MB-1 and SP-1. The highly erratic release in these two latter dispenser types may have been caused by the properties of the plasticizer or membrane in which the pheromone was immersed. It is also possible that the materials that the dispensers are made of may be more susceptible to weathering in the field. These assertions are speculative and cannot be substantiated by the release data alone.

In conclusion, we found the VCS to be well-suited for directly comparing codlemone release performance among dispenser types exposed to similar field-aging conditions. This system can accommodate a large number of collection chambers and can easily be adapted for use by pheromone dispenser manufacturers. We believe that this VCS can assist dispenser manufacturers to quickly evaluate pheromone release performance for new products before they are introduced into the market. This system can also provide rapid verification for growers of field-aged release performance when dispenser efficacy comes into question. However, this system could be improved considerably by making design changes to accommodate digital temperature and air-flow recording for more accurately investigating the influences of air-flow characteristics on chemical release. Such system improvements will further our knowledge of the effect of changing environment conditions on dispenser release performance.

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